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Emissions Assessment of Conventional Stationary Combustion Systems: Volume V: Industrial Combustion Sources

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Redondo Beach, CA

Prepared for

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EMISSIONS ASSESSMENT OF CONVENTIONAL STATIONARY COMBUSTION SYSTEMS:
VOLUME V: INDUSTRIAL COMBUSTION SOURCES

Prepared under the direction of the
Conventional Combustion Environmental Assessment Program

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16. ABSTRACT The report characterizes air emissions from industrial external combustion sources and is the last of a series of five reports characterizing emissions from conventional combustion sources. The emissions characterization of industrial combustion sources was based on a critical examination of existing data, followed by a modified Level 1 sampling and analysis approach to resolve data gaps. Tests were conducted at 32 external combustion sites. Emissions assessment results indicate that air emissions from these sources represent a potential environmental hazard. Criteria pollutant emissions, except for CO, from most of the source categories tested are environmentally significant. Particulate sulfate emissions from coal- and wood-fired sources and SO3 emissions from two coal-fired sources are also significant. In addition, emissions of several trace elements are of concern: As, Be, Cl, Co, Cr, Fe, K, Li, Na, Ni, P, and Pb from coal-fired external combustion sources; Ni, Cr, P, and V from distillate oil sources; and Cl, Cr, Na, Ni, Si, and V from residual oil sources. Several potentially hazardous POM compounds were tentatively identified in the emissions from solid-fuel-fired sources; however, further study is needed to positively identify the compounds.

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1.0 EXECUTIVE SUMMARY AND CONCLUSIONS

Emissions from industrial external combustion sources used for the purposes of electricity generation, production of process steam and space heating are characterized in the report. Emissions resulting from the direct firing of industrial process operations or from the use of fuel as feedstock were not considered. Emphasis was placed on the characterization of air emissions from flue gas stacks, although samples of ash from wood combustion were collected and analyzed during the study for the purpose of supplementing a limited data base.

1.1 PROGRAM METHODOLOGY

The approach to the characterization of emissions from industrial combustion sources involved a critical review of existing data, followed by a sampling and analysis program to fill gaps in the data base. Data acquired as a result of the measurement program, in combination with the existing data, were further evaluated. Data inadequacies identified at the completion of the current program are discussed with respect to the need for additional study. Specifically, the objectives of this program were:

- to compile and evaluate all available air emissions data on pollutants from selected industrial stationary conventional combustion processes,
- to acquire new emissions data from field tests,
- to characterize air emissions from selected stationary conventional combustion processes and ash from wood combustion, using combined data from existing sources and field tests, and
- to determine additional data needs, including specific areas of data uncertainty.

The emissions characterization was based on modified Level I sampling and analysis procedures, the principal modification being the use of gas chromatography/mass spectroscopy to analyze for polycyclic organic material (POM). Level I procedures use semiquantitative (plus or minus a factor of 3) techniques of sample collection and laboratory and field analysis to: (1) provide preliminary emissions data for waste streams and pollutants not adequately characterized; (2) identify potential problem areas; and (3) set priorities for waste streams and pollutants in those streams for further, more quantitative testing. Using the information from Level I, available resources can be directed toward Level II testing, which involves specific quantitative analysis of components of those streams that do contain significant pollutant levels. The data developed at Level II are used to identify control technology needs and to further define the environmental hazards associated with emissions.

1.2 SOURCE DESCRIPTION

Stationary external combustion sources used within the industrial sector for electricity generation, production of steam for process heating, and space heating can be classified according to the type of fuel used and furnace and boiler design. Fuels used in industrial combustion systems include bituminous coal, anthracite coal, lignite coal, wood, residual oil, distillate oil, and natural gas. Pulverized dry bottom furnaces and stoker furnaces are the major furnace designs used by the industrial sector for the combustion of bituminous coal. Stoker furnaces predominate for wood-fired combustion sources and for the combustion of lignite and anthracite coals. Although a large percentage of industrial boilers are cast iron systems, these systems constitute only about 7 percent of total industrial boiler capacity. Firetube boilers, in which the combustion gases pass through tubes submerged in water, make up about 24 percent of total industrial capacity. These units generally are smaller than about 21 GJ/hr* input capacity. Watertube boilers constitute about 69 percent of the industrial boiler capacity. In a watertube system the combustion gases transfer heat to tubes into which water is fed to be converted to steam. Boiler systems larger than about 53 GJ/hr input capacity and systems with steam pressures exceeding about 65 kPa are almost exclusively watertube systems.

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*One Btu = 1,055 Joules (J). Although it is EPA policy to use the metric system, this publication uses certain nonmetric units for convenience. A conversion table is presented in Appendix D.

There are approximately 500,000 industrial boilers in the United States with an estimated capacity of about 4,000 x 10^{12} J/hr. Natural gas is the primary fuel, accounting for about 63 percent of the total industrial fossil fuel use in 1978; while oil and coal account for about 18 percent and 15 percent, respectively. Wood and other miscellaneous fuels are minor fuel sources. Total fuel consumption by the industrial external combustion sources considered in this study was 8700 x 10^{15} J/yr in 1978, about 25 percent of total national fuel consumption by the stationary combustion sources studied in this program. The overall growth rate during the 1978 to 1985 period should be about 3 percent per year. Coal consumption by 1985 could account for 30 percent of industrial fuel use in 1985, if provisions of the National Energy Plan are fully implemented. This increase, however, could be a gross overestimate because of the influence of regulatory actions limiting, for example, sulfur content of the coal fuel.

Air, water, and solid waste pollutants are emitted from many sources constituting an industrial boiler facility. The major source of air emissions is flue gas emissions from stacks. Other potential sources of air emissions, depending on the size of the facility and the type of fuel burned, are ash handling and storage, fuel handling and storage, and drifts and vapors from cooling systems. Wastewater emission streams and sources of solid wastes vary in number and volume, depending again on facility size and type of fuel burned. Emphasis in this study was placed solely on air emissions from stacks, with the exception of the characterization of bottom ash and fly ash from the wood-fired systems tested in this study.

Air pollution control on industrial boilers is mainly directed at reducing particulate flue gas emissions from solid fuel-fired sources. The estimated overall efficiency of particulate removal in the industrial sector, based on data in the National Emissions Data System (NEDS), is 81 percent for pulverized units and 53 percent for stokers. Application of control measures for SO_x and NO_x is not extensive in the industrial sector, but will increase with the promulgation of regulations for control of such emissions from industrial boilers.

1.3 EXISTING EMISSIONS DATA BASE

This study emphasized gaseous and particulate emissions from industrial sources. Existing flue gas emissions data were evaluated before conducting the sampling and analysis program. As a result of the data evaluation effort, many data inadequacies were identified. The status of the existing data base can be summarized as follows.

- The existing data base for criteria pollutants* is generally adequate, with the exception of that for emissions from wood-fired combustion sources.
- The existing data base for particulate sulfate and sulfuric acid emissions is inadequate for the oil- and solid fuel-fired combustion source categories.
- The existing data base for particulates by size fractions and trace elements is adequate only for gas-fired sources.
- The existing data base for specific organics is inadequate for all industrial source categories.

As noted previously, industrial boilers are also sources of water pollution and solid waste. However, these sources, particularly in the case of large industrial boilers used for electricity generation, are similar to those at electric utilities. These sources of pollution were characterized for electric utilities earlier in this program, and the results can be found in Volume III of this program report series.

1.4 SOURCE MEASUREMENT PROGRAM

In order to overcome some of the deficiencies in the existing emissions data base, the following 32 external combustion systems were tested: 10 gas-fired, 3 distillate oil-fired, and 5 residual oil-fired boilers; 3 bituminous pulverized wet bottom and 2 bituminous pulverized dry bottom units; 3 bituminous stokers; and 5 wood-fired stokers. Specific sites were chosen based on the representativeness of the sites as measured against the important system characteristics within each source category, including system design, size, and age.

1.4.1 Level I Field Testing

The Source Assessment Sampling System (SASS) train, developed under contract to EPA, was used to collect both gaseous and particulate emissions in quantities sufficient for the wide range of analyses needed to adequately characterize emissions from the industrial combustion sources. The SASS train consists of a conventional heated probe, three cyclones and a filter mounted in a heated oven, a gas conditioning system, an XAD-2 polymer adsorbent trap, and a series of impingers. Particulate matter is size-fractionated and collected in the cyclones and on the filter, gaseous organics and some inorganics are collected by the XAD-2 adsorbent, and the remaining gaseous inorganics and trace elements are captured by the impingers. The train is run until at least 30 m^3 of gas has been collected. This criterion was established in conjunction with analytical technique sensitivities to ensure that any emission that would increase the ambient loading by more than 1 $\mu g/m^3$ would be detected. The cyclones were deleted for the gas- and oil-fired sites because particulate loadings were too low to provide weighable quantities of samples from each cyclone.

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*Criteria pollutants are those pollutants for which a National Ambient Air Quality Standard (NAAQS) exists, e.g., particulate, sulfur dioxide, nitrogen oxides, carbon monoxide and hydrocarbon. The criteria pollutant, lead, is categorized in this study as a trace element.

In addition to using the SASS train for stack gas sampling, other equipment was employed to collect those components that could not be analyzed from the train samples. A gas chromatograph (GC) with flame ionization detection was used in the field to analyze C_1-C_6 hydrocarbons collected in Tedlar gas sampling bags. Additionally, these samples were analyzed for CO, CO_2, O_2 and N_2 by GC using thermal conductivity detection. Field sampling for NO_X and SO_3 was also conducted at selected sites using a Method 7 train (40-CFR-60, Appendix A, Method 7) for NO_X and a controlled condensation sampling train for SO_3 collection.

1.4.2 Modified Level I Laboratory Analysis

A modified Level I sampling and analytical procedure was used in this emissions assessment program. Major deviations from Level I procedures included the use of gas chromatography/mass spectroscopy (GC/MS) for organic analyses, the combination of certain SASS train fractions before analysis and the deletion of inorganic analysis of SASS train samples collected from gas- and oil-fired sources. The combination and deletion guidelines were instituted as a result of low levels of pollutants found in the flue gases of previously tested gas- and oil-fired utility boilers and residential heating systems. Full details of the procedures used are presented in Section 4.

1.4.2.1 Inorganic Analyses--

Level I inorganic analysis was designed to identify all elemental species collected in the SASS train fractions and to provide semiquantitative data on the elemental distributions and total emission factors. The primary tool for Level I inorganic analysis is Spark Source Mass Spectrography (SSMS). SSMS data were supplemented with Atomic Absorption Spectrometry (AAS) data for Hg, As, and Sb, and with standard method determinations for sulfates.

The following SASS train fractions from the solid fuel-fired sources were analyzed for their elemental composition: (1) the cyclone catches, (2) the particulate filter, (3) the XAD-2 sorbent, and (4) a composite sample containing portions of the XAD-2 module condensate and HNO_3 rinse, and the first impinger solution. Fuel was also analyzed for the solid fuel- and oil-fired sources.

1.4.2.2 Organic Analyses--

Level I organic analysis provides data on volatile (C_7-C_{16}) and nonvolatile (>C_{16}) organic compounds to supplement data for gaseous organics (C_1-C_6) measured in the field. Organics in the particulate fractions, the XAD-2 sorbent, and XAD-2 module condensate trap were recovered by methylene chloride extraction. SASS train components including the tubing were carefully rinsed with methylene chloride or methylene chloride/acetone solvent to recover all organics collected in the SASS train. SASS train rinses and extracts recovered from the gas- and oil-fired sites were combined for analysis; however, samples collected from solid fuel-fired sources were analyzed separately.

Because all samples contain significant quantities of solvents from rinsing and are too dilute to detect organic compounds by the majority of instrumental techniques employed by Level I procedures, the first step in the analysis was to concentrate the sample fractions from as much as 1000 ml to 10 ml in a Kuderna-Danish apparatus in which rinse solvent is evaporated while the organics of interest are retained.* Kuderna-Danish concentrates were then evaluated by GC, gravimetric analysis, infrared spectrometry (IR), and sequential GC/MS.† The extent of the organic analysis is determined by the stack gas concentrations found for total organics (volatile and nonvolatile). If the total organics indicate a stack gas concentration below 500 μg/m³, further analysis is not conducted. If the concentration is above 500 μg/m³, a class fractionation by liquid chromatography is conducted followed by GC, gravimetric and IR analyses. Low resolution mass spectroscopy analysis was also conducted on individual fractions which contained an equivalent concentration of 500 μg/m³ or which were of special interest.

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*Kuderna-Danish is a glass apparatus for evaporating bulk amounts of solvents.

†The major modification in the Level I sampling and analysis procedure was the GC/MS analysis for POM.

1.4.3 Results

The results of the field measurement program for flue gas emissions from industrial sources, along with supplementary values obtained from the existing data base for certain pollutants, are presented in Table 1. Results of analyses of ash samples from wood-fired systems are also presented in the table. Also listed in Table 1 are ambient severity factors, defined as the ratio of the calculated maximum ground-level concentration of the pollutant species to the level at which a potential environmental hazard exists. An ambient severity factor of greater than 0.05 indicates a potential problem requiring further attention (see Appendix A for the rationale used to select 0.05 as the value indicative of a potentital environmental problem). For the ash samples collected during tests of the wood-fired sources, discharge severity, the ratio of the elemental concentration in the ash to the health Minimum Acute Toxicity Effluent (MATE) value of the element, was used as a measure of potential hazard. A discharge severity exceeding one is considered to warrant concern regarding the impact of emissions on health.

The particulate, elemental, and particulate sulfate emission factors shown in Table 1 are the mean values of those measured in this study. One bituminous, pulverized wet bottom unit and one bituminous stoker were controlled by electrostatic precipitators. Multiclones were used on the remaining bituminous coal-fired units, with the exception of one pulverized dry unit, which was controlled by a double alkali flue gas desulfurization (FGD) unit (measured particulate efficiency - 99.47 percent). Emissions from two wood-fired boilers were controlled by particulate scrubbers; the remaining three wood-fired units were uncontrolled. Emission factors for gas- and oil-fired units presented in the table represent uncontrolled emission factors. As noted

TABLE 1. SUMMARY OF EMISSIONS CHARACTERIZATION OF INDUSTRIAL COMBUSTION SOURCES

	Combustion source category									
	Gas-fired boilers		Distillate oil-fired boilers		Residual oil-fired boilers		Coal-fired bituminous pulverized dry bottom boilers		Coal-fired bituminous pulverized wet bottom[a] boilers	
Pollutant	Emission factor (ng/J)	Ambient severity factor[b]	Emission factor (ng/J)	Ambient severity factor[b]	Emission factor (ng/J)	Ambient severity factor[b]	Emission factor[a] (ng/J)	Ambient severity factor[b]	Emission factor[a] (ng/J)	Ambient severity factor[b]
Particulates	2	<0.01	6	<0.01	30	0.05	12	0.02	20	0.03
NO_x	70	0.35	70	0.35	170	0.85	350	1.8	586	2.9
SO_2	0.26	<0.01	106	0.11	464	0.52	766	0.85	766	0.85
CO	8	<0.01	15	<0.01	15	<0.01	20	<0.01	20	<0.01
HC	1	<0.01	3	0.01	3	0.01	6	0.02	6	0.02
Particulate sulfate[c]	-	-	-	-	-	-	1.8	0.15	0.12	3.2
SO_3	-	-	-	-	5.7	0.87	4.1	0.60	-	-
Trace elements										
Al	-	-	180	<0.01	175	<0.01	930	0.02	1100	0.03
As	-	-	4	<0.01	<1	<0.01	50	0.12	14	0.03
Ba	-	-	1	<0.01	<1	<0.01	21	<0.01	70	0.02
Be	-	-	<1	<0.01	<1	0.01	<1	0.03	<1	<0.01
Ca	-	-	75	<0.01	228	<0.01	70	<0.01	400	<0.01
Cd	-	-	1	<0.01	<1	<0.01	<1	<0.01	<1	<0.01
Co	-	-	4	0.01	11	0.03	20	0.05	6	0.01
Cr	-	-	24	0.06	29	0.07	28	0.07	5	0.01
Cu	-	-	38	<0.01	10	<0.01	22	<0.01	19	<0.01
Fe	-	-	380	0.01	55	<0.01	660	0.02	1400	0.03
K	-	-	85	<0.01	260	0.01	160	<0.01	200	0.01
Li	-	-	<1	<0.01	<1	0.01	<1	<0.01	<1	<0.01
Mn	-	-	42	<0.01	8	<0.01	62	<0.01	6	<0.01
Na	-	-	62	<0.01	1235	0.06	240	0.01	974	0.05
Ni	-	-	255	0.32	730	0.89	15	0.02	16	0.01
P	-	-	46	0.05	18	0.02	28	0.03	89	0.11
Pb	-	-	24	0.02	1	<0.01	6	<0.01	88	0.11
Si	-	-	735	<0.01	5790	0.07	1350	0.02	713	<0.01
V	-	-	195	0.05	365	0.09	15	<0.01	5	<0.01
Total POM	-	-	0.015	-	<0.001	-	ND	-	-	0.003

(continued)

TABLE 1 (continued)

Pollutant	Combustion source category									
					Ash from wood combustion					
	Coal-fired Bituminous stokers		Wood stokers		Bottom ash		Cinder ash		Scrubber ash	
	Emission factor[a] (ng/J)	Ambient severity factor[b]	Emission factor[a] (ng/J)	Ambient severity factor[b]	Concentration (ppm)	Discharge severity[d]	Concentration (ppm)	Discharge severity[d]	Concentration (ppm)	Discharge severity[d]
Particulates	84	0.1	70	0.11	-	-	-	-	-	-
NO_x	290	1.1	50	0.25	-	-	-	-	-	-
SO_2	766	0.64	65	0.07	-	-	-	-	-	-
CO	40	<0.01	400	<0.01	-	-	-	-	-	-
HC	20	0.05	100	0.36	-	-	-	-	-	-
Particulate sulfate	4.5	0.38	3.1	0.35	-	-	-	-	-	-
SO_3	-	-	-	-	-	-	-	-	-	-
Trace elements										
Al	890	0.02	577	0.01	11,270	0.70	9,700	0.61	8,900	0.56
As	144	0.35	12	0.03	10	0.19	7	1.4	18	0.36
Ba	66	0.02	90	0.21	1,640	1.6	2,800	28	560	0.56
Be	2.8	0.13	<1	0.01	<1	0.06	<1	0.01	<1	0.08
Ca	820	<0.01	14,280	1.8	119,000	2.5	416,670	8.7	110,000	2.3
Cd	<1	<0.01	3	<0.01	<1	0.03	1	0.10	<1	<0.01
Co	34	0.08	<1	<0.01	17	0.12	15	0.10	20	0.15
Cr	58	0.14	6	0.015	2,300	46	28	0.55	260	5.2
Cu	270	0.03	106	0.01	129	0.13	280	0.28	90	0.09
Fe	2,660	0.06	876	0.02	32,670	109	47,030	157	22,000	73
K	1,370	0.08	18,750	1.1	28,530	6.8	38,330	9.1	14,000	3.3
Li	13	0.07	3	0.03	6	0.08	5	0.08	7	0.10
Mn	37	<0.01	314	<0.01	9,230	185	4,900	98	5,000	112
Na	990	0.05	66	<0.01	4,330	0.03	12,100	0.08	4,200	0.03
Ni	184	0.22	29	0.04	185	4.1	94	2.1	140	3.1
P	810	1.0	1,190	1.5	9,770	3.3	5,620	1.9	6,200	2.1
Pb	127	0.10	50	0.04	23	0.46	52	1.0	30	0.60
Si	1,875	0.02	750	<0.01	91,330	3.0	140,670	4.7	75,000	2.5
V	54	0.01	5	<0.01	69	0.14	72	0.14	65	0.13
Total POM	0.18	-	0.18	-	ND	-	ND	-	-	0

[a] Controlled emissions of particulates, particulate sulfate, and trace elements.

[b] Ambient severity is defined as the ratio of the calculated maximum ground level concentration to the level at which a potential hazard exits. A value equal to or greater than 0.05 is considered significant.

[c] Determined turbimetrically following hot water extraction of sulfate from the collected particulate.

[d] Dishcarge severity is defined as the ratio of the concentration in the ash to the health MATE value of the pollutant. A value equal to or greater than 1.0 is considered significant.

- = Not measured.

ND = Not detected.

previously, the overall efficiency of particulate control in the industrial sector is 81 percent for pulverized units and 53 percent for stokers. Gas- and oil-fired units are essentially uncontrolled. Control measures for criteria pollutants other than particulates are not widespread in the industrial sector.

As can be seen from Table 1, the major criteria pollutants of concern are: particulates from residual oil sources and all uncontrolled solid fuel-fired units; NO_x from all source categories; SO_2 from oil- and solid fuel-fired sources, including wood-fired units (assuming a sulfur content of 0.1 percent and 95 percent conversion to SO_2); and HC from bituminous stokers and wood-fired boilers. Ambient severity factors are all greater than 0.05 for these pollutant/source combinations. Emissions of CO from all the combustion source categories tested do not represent an environmental problem.

Particulate sulfate and SO_3 emissions from the solid fuel-fired sources tested are associated with ambient severity factors in excess of 0.05 and, thus, represent a potential environmental hazard. Also, SO_3 emissions, measured in one test of a unit burning residual oil, are significant despite the use of a double alkali FGD unit to control emissions from this source. Although the SO_2 removal efficiency of this FGD unit was 97.5 percent, only 28.5 percent of the SO_3 was removed from the flue gas.

The trace element data shown in Table 1 indicate that many trace elements emitted by controlled bituminous coal-fired sources are of concern. Elements of greatest concern appear to be arsenic, beryllium, cobalt, chromium, iron, potassium, lithium, sodium, nickel, phosphorus, lead, and silicon. Chlorine, on the basis of its concentration in coal, and other elements in addition to those listed above, may also be of concern because of variations in the elemental content of bituminous coals. Because many industrial sources are totally uncontrolled or only partially controlled, further consideration of trace element emissions is warranted.

Trace element emissions of concern from the wood-fired sources tested include barium, calcium, potassium and phosphorus. Ambient severity factors calculated from the mean of the emission factor from these sources exceed 0.05 for these elements. Overall removal efficiency of particulates and nonvolatile trace elements from the five wood-fired units tested is estimated to be 36 percent.

Chromium, nickel, phosphorus, and vanadium emissions from distillate oil-fired sources, and chromium, sodium, nickel, silicon, and vanadium emissions from residual oil-fired sources are significant. Ambient severity factors, based on mean emission factors measured in this study, exceed 0.05. In addition, information in the existing data base indicates that ambient severity factors can exceed 0.05 for chlorine, cobalt, fluorine and magnesium emissions from residual oil-fired boilers.

POM emissions from bituminous stokers and wood-fired boilers are potentially significant. Mean emission factors for total POM were 180 and 210 pg/J, respectively, for these sources. Although no active carcinogens were positively identified and ambient severity factors for most compounds were less than 0.05, the possible presence of benzo(a)pyrene in significant amounts was indicated in the emissions of two wood-fired boilers and one bituminous stoker. Level II testing is needed to provide positive identification of the POM compounds emitted from these sources.

The samples of ash collected from the wood-fired sources were analyzed for trace elements by SSMS and for organics; TCO, gravimetric organics, and POM. Three types of samples were collected; bottom ash, cinder ash collected downstream of the combustion chamber, and fly ash collected by a particulate scrubber control device. Discharge severity, the ratio of the elemental concentration in the ash to the elemental health MATE value for solids, was used to evaluate the impact of ash disposal. A value in excess of one indicates that a potential environmental problem exists.

As shown in Table 1, the discharge severity is in excess of one for several trace elements. Elements of concern in bottom ash are barium, calcium, chromium, iron, potassium, manganese, nickel, phosphorus and silicon. For cinder ash, discharges severities in excess of one were found for arsenic, barium, calcium, iron, potassium, manganese, nickel, phosphorus, and silicon. Fly ash elements of concern include calcium, chromium, iron, potassium, manganese, nickel, phosphorus and silicon. If ecological effects are considered, several other elements will warrant concern because the ecology Discharge Multimedia Environmental Goal (DMEG) or MATE values for the pollutants of interest are generally lower than those for health. DMEG values are equivalent to MATE values and are derived through a series of models which use available data relating to properties of chemical toxicants for both health and ecological effects. DMEG values represent concentrations that will cause minimal adverse effects on either a human (health DMEG) or an ecological receptor (ecological DMEG).

As anticipated, TCO and gravimetric organics were not present in significant amounts in bottom ash. Organics were generally found in greater amounts in cinder ash and fly ash, but are not of environmental concern. Although POM compounds were not found in the samples of bottom ash and cinder ash, they were found in the one sample of fly ash collected by a particulate scrubber. The POM compounds were identical to POM compounds collected downstream of the scrubber by the SASS train at this site. Further, the relative distribution of these compounds in the scrubber ash and in the SASS samples was similar. Based on this, wood fly ash will present a definite hazard at sites emitting POM compounds such as benzo(a)pyrene. The compound benzo(a)pyrene was tentatively identified in the flue gas emissions of two uncontrolled wood-fired boilers during this study.

1.5 CONCLUSIONS

Several conclusions, listed as follows, can be drawn from the characterization of emissions from industrial external combustion source:

- Industrial external combustion sources in 1978 accounted for 25, 15, 9, 24 and 28 percent, respectively, of total nationwide emissions of particulates, NO_x, SO_2, CO, and HC emissions from external combustion sources.
- Flue gas emissions of NO_x from industrial boilers are environmentally significant. Ambient severity factors exceeded 0.05 for all of the source categories tested in this study, ranging from 0.25 for wood-fired stokers to 2.9 for bituminous, pulverized wet bottom units.
- Flue gas emissions of SO_2 from the residual oil- and bituminous coal-fired sources are associated with ambient severity factors greater than 0.05 and, thus, are of environmental concern. The calculated SO_2 ambient severity factor of 0.07 for wood, shown in Table 1, is based on a fuel sulfur content of 0.1 percent. Normally the wood sulfur content will be lower than the assumed value of 0.1 percent and emissions from wood fuels containing

less than 0.07 percent sulfur would not be of concern. Ambient severity factors for particulate sulfate from bituminous coal and wood combustion, and for SO_3 from the two source categories tested, bituminous, pulverized dry bottom boilers and residual oil boilers, are in excess of 0.05 and warrant concern.

- Flue gas emissions of CO from industrial sources are of little concern. Ambient severity factors are less than 0.01 for all source categories.
- Flue gas emissions of HC are significant for bituminous stokers and wood boilers; ambient severity factors determined in this study are 0.05 and 0.35, respectively.
- Flue gas emissions of particulate from uncontrolled solid fuel-fired sources are of definite concern. Uncontrolled emissions of particulates from residual oil combustion (ambient severity factor of 0.05) may also be significant. Well controlled sources are not expected to be a problem. High efficiency devices, such as ESPs, should adequately control particulate emissions from large bituminous pulverized units and stokers. Ambient severity factors less than 0.05 are achievable with control devices with efficiencies of 80 to 90 percent for wood-fired units of 50×10^9 J/hr input capacity.
- Particle size distribution data for particulate emissions from solid fuel-fired boilers are inadequate. The data generally exhibited high variability. Further study of source category/control device combinations is needed.
- Trace element emissions from controlled bituminous coal combustion sources are of concern. Bituminous stokers, probably because of less efficient control of particulates, were the largest emitters of trace elements and particulates. Elements of principle concern are arsenic, beryllium, chlorine, cobalt, chromium, iron, potassium, lithium, sodium, nickel, phosphorus, and lead.
- Trace element emissions of concern from wood-fired boilers are barium, calcium, potassium, and phosphorus. Mean ambient severity factors exceed 0.05.
- For distillate oil sources trace element emissions of concern are chromium, nickel, phosphorus, and vanadium; for residual oil sources chlorine, chromium, sodium, nickel, silicon and vanadium are also associated with mean ambient severity factors in excess of 0.05 and, thus, are environmentally significant.

- Analysis of organic emissions from industrial sites indicates that the principal organic constituents are esters, ethers, glycols and aliphatic and aromatic hydrocarbons. The most prevalent constituents are generally associated with MATE values in the 10 to 1000 mg/m^3 range. Ambient severity factors will not exceed 0.05 at these MATE levels. However, more detailed Level II analysis would be required to definitely identify compounds and establish their environmental significance.

- Flue gas emissions of POM from gas-fired sources were not significant. Compounds identified in highest concentrations were naphthalene and phenanthrene. The data base for POM emissions from gas-fired industrial sources is adequate.

- POM emissions from oil-fired sources were not significant. Biphenyl was emitted in small amounts from two residual oil-fired boilers but the associated ambient severity factor was less than 0.001. The POM data base for oil-fired sources is adequate.

- POM compounds of potential environmental significance may be present in the flue gas emissions from bituminous stokers. and wood-fired boilers. A compound, tentatively identified as benzo(a)pyrene, was found at some of these sites. Phenanthrene was also emitted in significant amounts from one of the wood-fired boilers. Level II GC/MS analysis is required to positively identify POM compounds and to establish the impact of the POM emissions from these source categories.

- The disposal of fly ash from wood combustion poses a potential hazard. Compounds, such as benzo(a)pyrene, if present in flue gas emissions, could be collected by the control device. The discharge severity of this compound in the ash could well exceed unity. In addition, the discharge severities for several trace elements are appreciably greater than unity.

2.0 INTRODUCTION

The combustion of common fuels - coal, oil, gas, and wood - in conventional stationary systems for heating and power generation is one of the largest and most widespread sources of environmental pollution. Combustion of these fuels affects air, water, and land. In a preliminary assessment of the significance of stationary combustion systems as sources of pollution, it was estimated that these combustion sources contribute a major portion of the total manmade emissions of nitrogen oxides, sulfur dioxide, and particulate matter.[1] Further, many of the combustion processes and associated pollution control technologies also produce solid wastes, in the form of ash and sludge, that present disposal problems. Leaching of chemical compounds and heavy metals from fuel or waste material, as well as direct discharges of wastewater streams, may result in contamination of water resources. Assessment of the environmental impacts is complicated by multimedia effects, as pollutants merge with or pass between environmental media. For example, removal of sulfur dioxide and particulate matter from flue gases significantly increases the amount of solid wastes requiring disposal.

The U.S. Environmental Protection Agency (EPA) has long been active in regulating the release of pollutants from stationary conventional combustion processes. The involvement has included characterizing emission streams, researching on the health and ecological effects of combustion pollutants, developing and demonstrating pollution control technologies, and setting and enforcing environmental standards. Much of the earlier work on combustion pollutant characterization, however, was focused on the three major air pollutants - sulfur dioxide, nitrogen oxides, and particulate matter - and the subsequent development of control technologies and standards for these pollutants. As a consequence, the early characterization work was limited in scope and did not adequately address the emissions of other potentially hazardous pollutants or the multimedia aspects of combustion emissions.

These observations were confirmed in the preliminary assessment study,[1] which identified the inadequate characterization of flue gas emissions of trace elements, sulfates, particulate matter by size fraction, and polycyclic organic matter (POM). In addition, the same study also identified the general inadequacy of the data base characterizing air emissions from cooling towers and coal storage piles, and wastewater effluents and solid wastes from combustion processes.

From the above discussion, it is apparent that much of the data describing pollutant types and quantities released from stationary conventional combustion processes were unavailable. A comprehensive characterization of emissions from these processes, therefore, was needed as a basis for identifying the pollutants of concern, for estimating the total quantities of pollutants emitted, for assessing the impacts of pollutant emissions on health and the environment, and for evaluating the need for control technology development. In response to the need for a comprehensive characterization, the EPA's Industrail Environmental Research Laboratory at Research Triangle Park (IERL-RTP) in North Carolina established the Emissions Assessment of Conventional Combustion Systems program as one of the primary efforts for filling the identified data gaps. Specifically, the objectives of this program are:

- Compilation and evaluation of all available emissions data on pollutants from selected stationary conventional combustion processes.
- Acquisition of needed new emissions data from field tests.
- Characterization of air emissions, wastewater effluents, and solid wastes generated from selected stationary conventional combustion processes, using combined data from existing sources and field tests.
- Determination of additional data needs, including specific areas of data uncertainty.

Because of the comprehensive characterization requirement, the assessment process in the current program is based on a critical examination of exising data, followed by a phased sampling approach to fill data gaps. In the first phase, sampling and analysis procedures are used to provide results accurate to a factor of 3 so that preliminary assessments can be made and problem areas identified. The methodology employed is similar to the Level I sampling and analysis procedures developed under the direction of IERL; a major addition being that GC/MS analysis for POM is performed on the samples collected in this program. Evaluation of results from the first phase will determine all waste stream/pollutant combinations requiring a more detailed and accurate Level II sampling and analysis program. In terms of major potential benefits, the characterization of combustion source emissions from this program will allow EPA to determine the environmental acceptability of combustion wastes streams and pollutants and the need for control of environmentally unacceptable pollutants.

The combustion source types to be assessed in this program have been selected because of their relevance to emissions and because they are among the largest, potentially largest, or most numerous (in use) of existing combustion source types. A total of 51 source types have been selected for study. Selected source types have been classified under the following principal categories:

(1) Electricity generation - external combustion
(2) Industrial - external combustion
(3) Electricity generation and industrial - internal combustion
(4) Commercial/institutional - space heating and internal combustion
(5) Residential - space heating

These five principal categories have been further divided into subcategories based on fuel type, furnace design, and firing method. The subcategorization is needed because of the differences in the emission characteristics of combustion source types.

This program report is the fifth in a series of five group/category reports, and is concerned with the characterization of emissions from industrail combustion sources. The main purposes of this report are to discuss data evaluation and test results, and to provide in a single document, best estimates of emission factors for stack gas effluents from industrial combustion sources. These emission estimates were derived using combined data from existing information sources and field tests conducted in the current program. The report also provides estimates of nationwide flue gas emissions from industrial combustion sources. and identifies major gaps in emissions data. As such, information contained in the report can be used for:

- Compiling emission factors for pollutants for which no existing data were available.
- Upgrading existing emission factors for pollutants.
- Performing environmental assessments of industrial combustion sources.
- Determining the nationwide burden of emissions from industrial combustion sources.
- Evaluating the need for control technology development, based on analysis of the environmental impacts of uncontrolled and controlled emissions.
- Planning future Level II field tests to provide critical data needs.
- Providing input to the development of emission standards.

A total of seven industrial combustion source types are considered:*

2.1.11.1.0	External combustion, bituminous, pulverized dry
2.1.11.2.0	External combustion, bituminous, pulverized wet
2.1.11.6.0	External combustion, bituminous, spreader stoker
2.1.42.4.0	External combustion, wood, stoker
2.1.21.0.2	External combustion, residual oil
2.1.22.0.2	External combustion, distillate oil
2.1.30.0.0	External combustion, natural gas

The approach taken in this emissions characterization of industrial combustion sources is similar to that taken to characterize other combustion source types. First, available information concerning the process and population characteristics of the combustion sources and their emissions was assembled and assessed to determine the adequacy of the available data base. Sampling and analysis were then conducted at selected representative sites to fill identified data gaps in the existing data base. The results were evaluated to determine the need for and type of additional sampling and analysis, and to identify the environmentally significant substances emitted from industrial combustion sources. Emissions data obtained from the sampling and analysis program were combined with existing emissions data to provide estimates of current and future nationwide emissions of pollutants from industrial combustion sources. Appendix A describes the criteria for evaluating the adequacy of emission data. The data reduction procedure is presented in Appendix B. Finally, detailed tabulations of the existing data base are presented in Appendix C.

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*The I.D. Code referes to the classification code used in Reference 1.

3.0 SOURCE DESCRIPTION

The primary use of fuel in the industrial sector is for the production of steam which is then used for process heating, electricity generation, or space heating. Fuels used for this purpose include natural gas, oil, coal, wood, and waste products such as process or refinery gas, and bagasse. Natural gas and oil are also used in stationary internal combustion engines to produce electricity, and as feedstocks for various chemical processes. In addition, natural gas, oil, and process and refinery gases are often used for direct process heating.

This study is concerned with the characterization of emissions from the use of natural gas, oil, coal, and wood in industrial boilers. These boilers have a wide range of capacities and operate under a wide range of conditions. Although industrial boilers are sometimes defined as those boilers in the 10 to 500 GJ/hr size range, units as small as 0.4 GJ/hr and as large as 1500 GJ/hr in capacity are used in the industrial sector. Boiler steam temperatures range from 100°C to 500°C. To provide an understanding of the emissions associated with industrial boilers, this section presents an overview of the industrial boiler population with brief descriptions of industry size and geographic distribution; fuel consumption; combustion system design, size distribution and age; control system application; and trends.

3.1 SIZE OF THE INDUSTRY AND GEOGRAPHIC DISTRIBUTION

Table 2 compares natural gas, oil, coal, and other fuel use in the industrial sector with consumptions in the commercial, residential, and electric utility sectors for the year 1978. As shown in the table, the industrial sector accounts for approximately 25 percent of total fuel use. Natural gas is the primary fuel in the industrial sector, accounting for about 63 percent of the total fossil fuel use in 1978; while oil and coal account for about 18 percent and 15 percent, respectively. Wood, bagasse, and process and refinery gases are minor fuel sources. Approximately 72 percent of the energy derived from fossil fuels in the industrial sector was used to provide steam for process heat, while about 15 percent was used for electricity generation, and 14 percent was used for space heating.[5]

TABLE 2. U.S. FUEL CONSUMPTION IN THE UTILITY, INDUSTRIAL, COMMERCIAL, AND RESIDENTIAL SECTORS IN 1978

	Annual consumption (10^{18} Joules)			
Fuel	Utility	Industrial	Commercial	Residential
Natural gas	2.56	6.49	2.20	3.90
Petroleum	4.09	1.78[a]	2.60	2.53
Coal	11.46	1.54[b]	0.14	0.21
Other	0.01	0.45	0.10	0.05
Total	18.12	10.26	5.04	6.69

[a] Excludes oil company use.

[b] Excludes use for coke production.

Source: References 2, 3, and 4.

Estimates of total fuel consumption in the industrial sector are shwon in Table 3 for the period 1974 through 1978. This table shows an overall increase in industrial fuel consumption of about 3 percent per year. This growth is expected to continue through 1985.

TABLE 3. FUEL CONSUMPTION TRENDS IN THE INDUSTRIAL SECTOR

	Annual consumption (10^{18} Joules)				
	1974	1975	1976	1977	1978
Natural gas	5.92	6.12	6.51	6.45	6.49
Distillate oil[a]	0.26	0.26	0.32	0.39	0.38
Residual oil[a]	0.93	0.75	0.99	1.11	1.40
Coal[b]	1.60	1.36	1.35	1.50	1.54
Other	0.27	0.30	0.35	0.40	0.45
Total	8.98	8.79	9.52	9.85	10.26

[a] Excludes oil company use.

[b] Excludes use for coke production.

Source: References 2, 3, and 4.

Figures 1 through 3 illustrate 1978 regional consumption of gas, oil, and coal, respectively, in the industrial sector. For each type of fuel, the percentages of total U.S. industrial consumption are shown for states where consumption in the industrial sector exceeded 1 percent of the U.S. total. States in which industrial consumption exceeded 5 percent of the U.S. total are shaded. These figures show that consumption of all fuels, especially coal, was relatively high in the industrialized north central states; and that natural gas consumption was relatively high in the gas producing southern states of Texas and Louisiana, and in California.

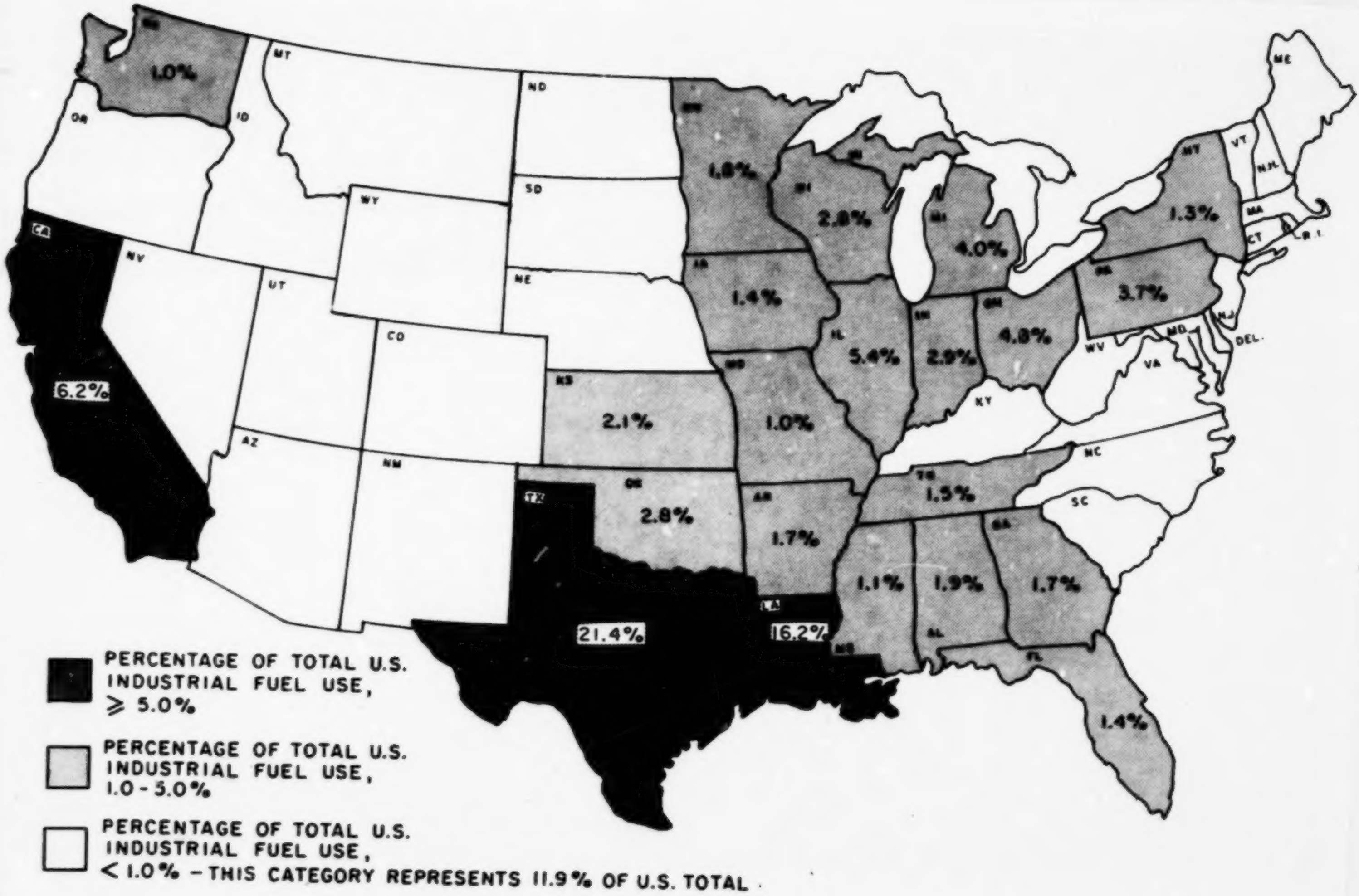
The distribution of industrial fuel consumption in 1978 with respect to (1) external and internal combustion, (2) fuel type, and (3) fuel firing method is estimated in Table 4. The various fuel firing systems shown in the table are described in the following section. Increases are expected in the use of coal and refuse fuels.

3.2 CHARACTERISTICS OF COMBUSTION EQUIPMENT

A typical steam producing external combustion system consists of a combustion chamber, in which fuel and air are mixed and caused to react, and a heat exchanger, or boiler, which transfers heat from the fuel combustion products to water, causing the production of steam. A system is generally classified according to the fuel firing method, and the type of boiler used, which are generally independent of one another. This section describes firing techniques and boiler systems typically used in the industrial sector.

3.2.1 Fuel Firing Methods

The fuel firing techniques used in a combustion system affects the degree of mixing between the fuel and combustion air, and, in the case of liquid and solid fuels, the fuel surface area exposed to the combustion air. Thus, for all fuels and especially for liquid and solid fuels, the firing method can have an impact on emissions of incomplete combustion products, including CO, hydrocarbons, and particulate soot (unburned carbon). For coal and other solid fuels, the firing method can influence the amount of inert matter which becomes entrained in exhaust gases.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LA
16.2%
WI
2.8%
MI
4.0%
IL
5.4%
IN
2.9%
OH
4.8%
KY
TN
1.5%
MS
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AL
1.9%
GA
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FL
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NY
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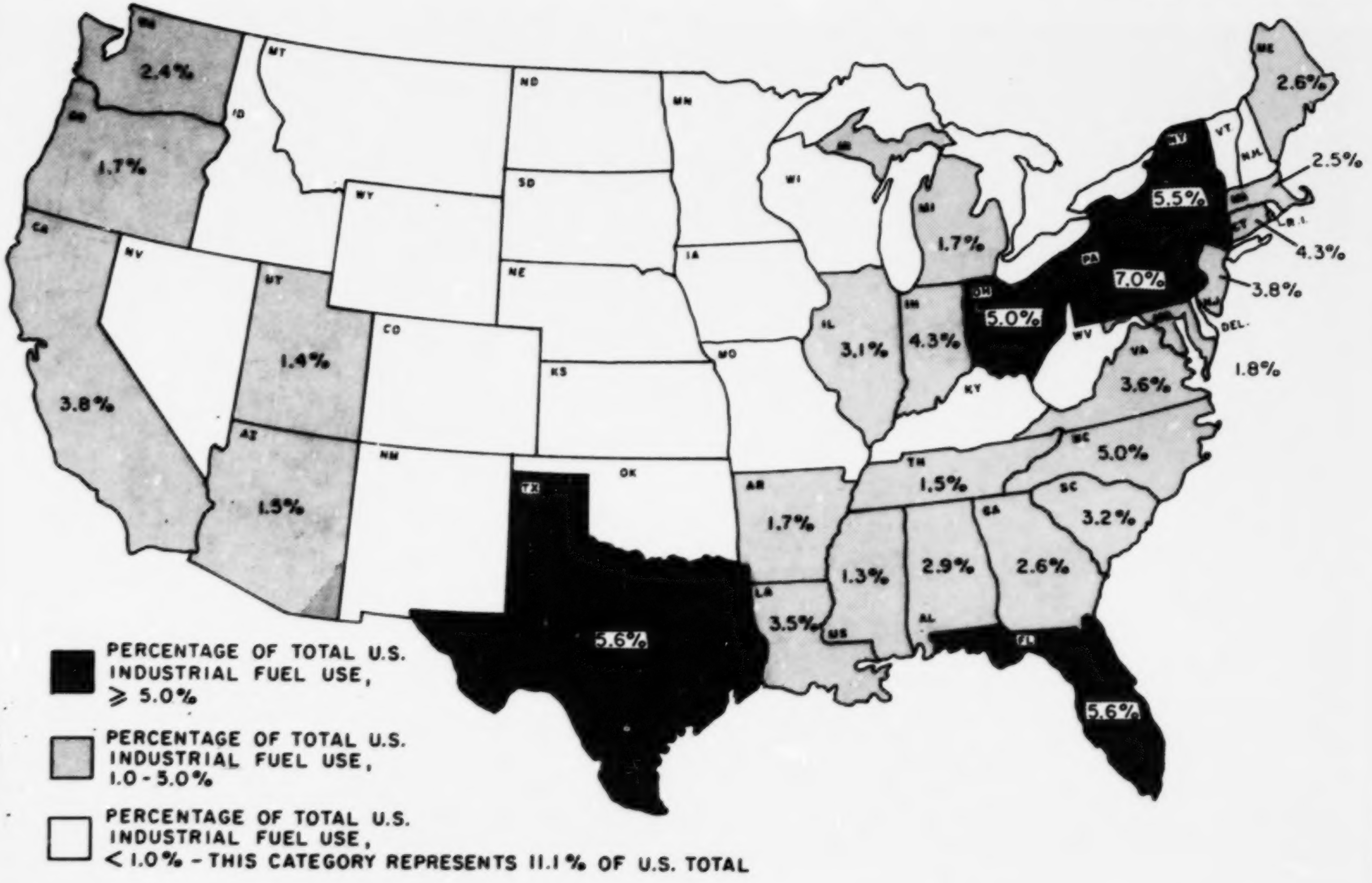
VT
N.H.
ME
MA
CT
R.I.
PERCENTAGE OF TOTAL U.S. INDUSTRIAL FUEL USE, ≥ 5.0%
PERCENTAGE OF TOTAL U.S. INDUSTRIAL FUEL USE, 1.0 - 5.0%
PERCENTAGE OF TOTAL U.S. INDUSTRIAL FUEL USE, < 1.0% - THIS CATEGORY REPRESENTS 11.9% OF U.S. TOTAL

Figure 1. Regional industrial consumption of natural gas, 1978.


WA
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WI
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MS
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AL
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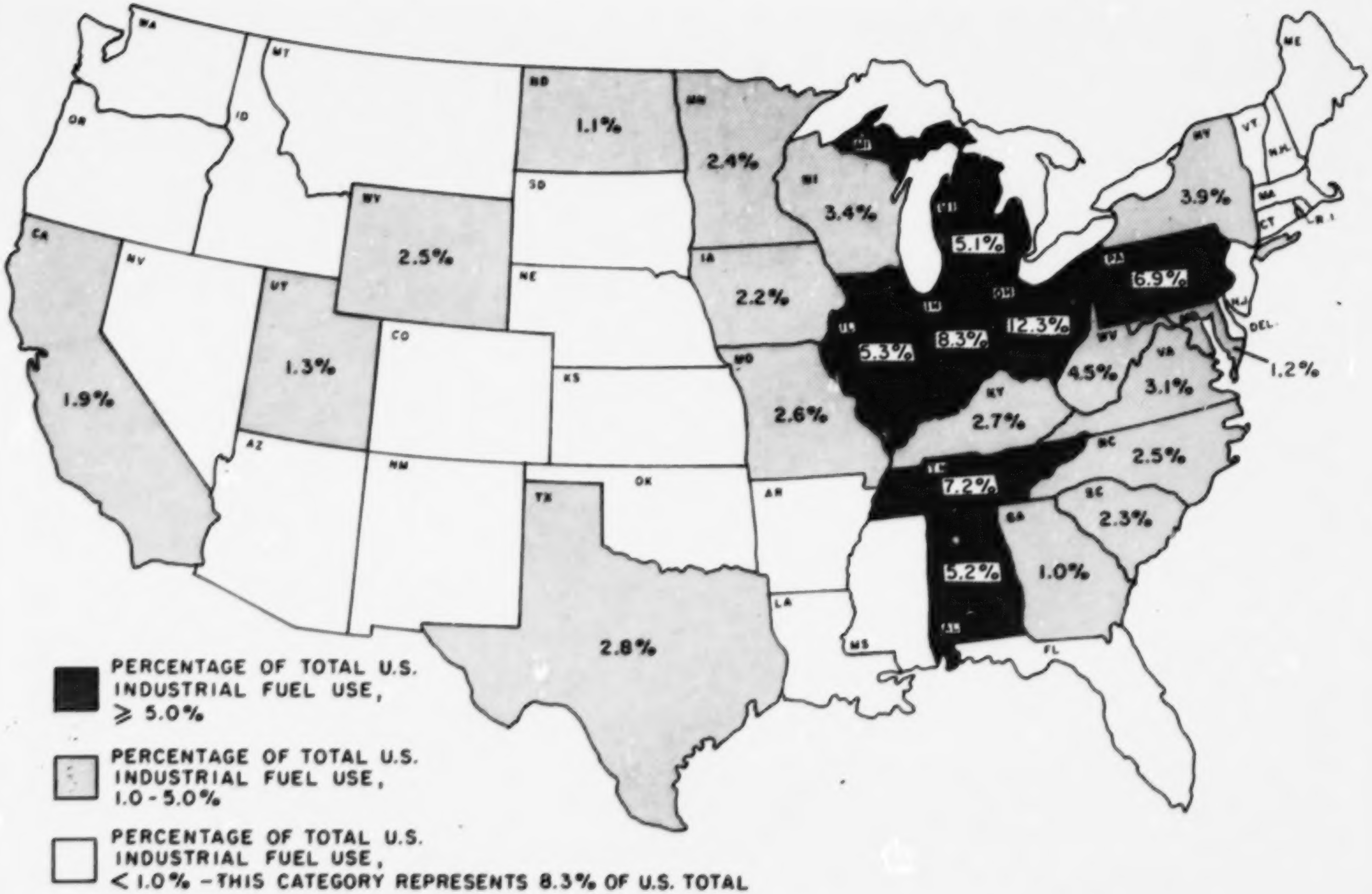
GA
2.6%
FL
5.6%
SC
3.2%
NC
5.0%
VA
3.6%
WV
PA
7.0%
NY
5.5%
VT
N.H.
ME
2.6%
MA
2.5%
R.I.
CT
4.3%
NJ
3.8%
DEL.
MD
1.8%
PERCENTAGE OF TOTAL U.S. INDUSTRIAL FUEL USE, ≥ 5.0%
PERCENTAGE OF TOTAL U.S. INDUSTRIAL FUEL USE, 1.0 - 3.0%
PERCENTAGE OF TOTAL U.S. INDUSTRIAL FUEL USE, < 1.0% - THIS CATEGORY REPRESENTS 11.1% OF U.S. TOTAL

Figure 2. Regional industrial consumption of distillate and residual oil, 1978.

Source: Reference 2.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12.3%
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7.2%
5.2%
1.0%
2.3%
2.5%
3.1%
4.5%
6.9%
3.9%
1.2%
PERCENTAGE OF TOTAL U.S. INDUSTRIAL FUEL USE, ≥ 5.0%
PERCENTAGE OF TOTAL U.S. INDUSTRIAL FUEL USE, 1.0 - 5.0%
PERCENTAGE OF TOTAL U.S. INDUSTRIAL FUEL USE, < 1.0% - THIS CATEGORY REPRESENTS 8.3% OF U.S. TOTAL

Figure 3. Regional industrial consumption of coal (bituminous and lignite); 1978

Source: Reference 1.

TABLE 4. ESTIMATED INDUSTRIAL FUEL USE BY COMBUSTION SYSTEM, 1978

Source category	Fuel used, (PJ/yr)
Industrial	10,260
External combustion	8,690
Coal	1,540
Bituminous	1,490
Pulverized, dry	730
Pulverized, wet	150
Cyclone	40
Spreader stokers	510
Other stokers	60
Anthracite	10
All stokers	10
Lignite	40
Spreader stokers	40
Petroleum	1,710
Residual oil	1,400
Tangential firing	170
Other	1,230
Distillate oil	310
Tangential firing	50
Other	260
Gas	4,990
Tangential firing	500
Other	4,490
Other	450
Wood/Bark	420
Bagasse	30
Internal combustion	1,570
Distillate oil	70
Gas	1,500

Source: References 1 through 7.

3.2.1.1 Gas Burners--

Because natural gas can be mixed easily with air, gas burners are considerably simpler than those used for oil or solid fuels. Natural gas is generally mixed with a fraction of the air necessary for complete combustion before being fed to the combustion chamber. The air mixed with the gas at this stage is called primary air. The gas mixture enters the combustion chamber either through nozzles or through perforated rings. Upon entering the chamber, the gas mixture is ignited and mixes with secondary air, which makes up the remainder of air necessary for complete combustion.

3.2.1.2 Atomization Methods for Oil-Fired Systems--

In order to maximize the surface area of oil exposed to air in industrial combustion systems, measures are taken to atomize oil as it enters the combustion chamber. Four basic methods of oil firing are currently in use: air, steam, and mechanical; and rotary cup. Particulate emissions from air atomized systems are typically lower than emissions from systems using other techniques.[8]

In air atomization systems, oil is fed to the combustion chamber through a central tube of a nozzle, and pressurized air is fed through an annulus around the oil passageway. The air and oil streams are combined either inside the nozzle, or allowed to mix after leaving the nozzle. The pressure drop across the nozzle causes turbulent mixing of the oil and atomizing air, resulting in the formation of fine oil droplets. The droplet stream ignites and mixes with secondary combustion air in the combustion chamber.

Steam atomized burners operate under the same principles as air atomized burners, except that high pressure steam, rather than pressurized air, is used to atomize the oil. Particulate emissions from steam atomized systems generally exceed emissions from air atomized systems by a factor of about three.[8] Steam atomized systems are generally used when high pressure steam is more readily available than pressurized air.

In mechanical atomization systems, pressurized oil is fed to the combustion chamber through one or more orifices. Oil droplets are given angular momentum as they leave these orifices. This angular momentum causes the droplets to break up into finer sizes. Particulate emissions from these systems are typically higher than emissions from air or steam atomized systems.[8] However, mechanical atomization systems are simpler and generally easier to maintain than air or steam atomization systems.

Rotary cup systems feed oil to the smaller end of a rotating cone, the larger end of which is exposed to the combustion chamber. Centrifugal forces cause the oil to form a thin film on the wall of the cone. The oil migrates to the lip of the cone, and is dispersed into the combustion chamber in the form of fine droplets. Rotary cup systems have high maintenance requirements relative to other atomization systems, and are therefore not generally in use in newer boilers.

3.2.1.3 Coal-Firing Methods--

Coal-firing techniques can be divided into two major groups: stoker firing and suspension firing. Stoker firing systems can be further divided into three groups: underfeed stokers, overfeed stokers, and spreader stokers. Suspension firing systems include pulverized coal-firing and cyclone systems.

In an underfeed stoker, coal is fed to the bottom of a fuel bed, where moisture and volatiles are driven off and the coal is coked. The volatiles rise through the bed and undergo combustion above the bed. The coked coal is forced to the top of the bed by newly fed coal and spills out of the bed onto side grates, where combustion is completed. Combustion air is supplied at the side grates; also overfire air is often supplied to the flame zone above the bed. Underfeed stokers generally are used to burn Eastern coking bituminous coal or anthracite, crushed to about 0.6 to 3.2 cm in diameter. They account for roughly 24 percent of total coal-fired industrial combustion system capacity.

In an overfeed stoker, coal is fed onto a continuous conveyor called a traveling grate. The grate carries the coal under an adjustable gate and through the furnace chamber, where combustion air is fed through the bottom of the grate. The coal burns as it moves across the furnace, and ash particles fall to the bottom of the furnace at the end of the grate. Overfeed stokers can burn a wide variety of coals, with the exception of coking bituminous coals, which mat and restrict airflow through the grate. In addition to coal, overfeed stokers can be designed to burn wood or other solid fuels. They account for roughly 8 percent of total coal-fired industrial combustion system capacity.

In a spreader stoker, feeders distribute coal uniformly over the traveling grate. Combustion air is provided both over and under the grate. Captured flyash is also recycled. Spreader stokers can be used to burn almost any type of coal or solid fuel, including wood, wood waste products, and bagasse. Coking qualities of coals used in spreader stokers have little effect on system performance. Spreader stokers represent approximately 23 percent of total coal-fired industrial combustion system capacity.

Pulverized coal-fired systems constitute approximately 33 percent of total U.S. industrial coal-fired boiler capacity. These systems use coal pulverized to the consistency of fine powder. This coal is generally suspended in primary air before being fed to the combustion chamber, where it is ignited and mixed with secondary combustion air. Pulverized coal furnaces are further classified as dry bottom or wet bottom systems depending on the ash removal technique used. In dry bottom furnaces, coals with high fusion temperature are burned and dry ash removal techniques are used, while, in wet bottom furnaces, coals with low fusion temperatures are used and ash can be removed through a slag tap. In the industrial sector, dry bottom pulverized coal-fired systems are much more widely used than wet bottom systems.

Cyclone furnaces are not as widely used in the industrial sector as pulverized coal-fired systems or stoker systems (Table 4). These furnaces are used to burn low fusion temperature coal that has been crushed to a maximum particle size of about 4.75 mm (4 mesh). The coal is fed tangentially, with primary air, to a horizontal cylindrical chamber. In the furnace, smaller coal particles are burned in suspension, while, because of the tangential firing method, larger particles are forced against the outer wall of the chamber. Ash is also forced against the outer wall, where, because of its low fusion temperature. it forms a molten layer of slag and causes larger coal particles to adhere to the combustion chamber wall until they are burned instead of becoming entrained in exhaust gases leaving the combustion chamber.

In all coal-fired combustion systems, particulate emissions are directly related to the ash content of the coal used. However, the extent to which the ash becomes entrained in exhaust gases is dependent on the coal-firing methods. Particulate emission factors, based on the ash content of coal, have been published by EPA for various coal-firing techniques.[9] For spreader stokers, other stokers, pulverized coal fired systems, and cyclone systems , particulate emission factors are 13A, 5A, 16A and 2A pounds per ton of coal, respectively. The ash content of coal in percent is denoted by A; an emission factor of 20A represents 100 percent entrainment of coal ash content in the flue gases assuming complete combustion of all combustible matter.

3.2.1.4 Wood-Firing Methods--

Firing methods for wood-burning boilers include spreader stokers, overfeed stokers, underfeed stokers, dutch ovens, suspension-firings, and fluidized-bed combustion (FBC). The various stoker and suspension firing methods designs are essentially the same as those described in Section 3.2.1.3 for coal-fired boilers. The dutch oven design is basically a refractory-lined, rectangular box into which the wood fuel is dropped through a feed chute. The fuel burns on a fixed grate that is sometimes water-cooled. Ash falls through the grate and collects in an ash pit. The FBC design uses a bed of inert particles through which air is blown so that the bed behaves as a fluid. Wood fuel enters in the space above the bed and burns both in suspension and in the bed. The ash is removed from the bottom of the combustion chamber where it collects after falling through the bed.

The vast majority of installed wood-fired boilers are spreader stokers and dutch ovens. The latter were the standard design prior to the 1950s, when they began to be replaced by stokers in new installations. Dutch ovens are still quite common, but new ones are rarely, if ever, built. The most common design of new boilers is the spreader stoker. The other stoker designs and FBC are relatively rare.

Wood-burning boilers are rarely fired with 100 percent wood fuel. They are usually equipped to burn a fossil fuel as well, with oil and natural gas being the most common alternative fuels. The oil or natural gas is usually used to start up the boiler or carry most of the steam load during periods when the wood supply is interrupted. When coal is used as a supplemental fuel, it is almost continuously co-fired with the wood.

3.2.2 Heat Transfer Systems

In the industrial sector, three boiler types are currently in use: cast iron boilers, firetube boilers, and watertube boilers.

3.2.2.1 Cast Iron Boilers--

Although a large percentage by number of industrial boilers are cast iron systems, these systems comprise only about 7 percent of the total U.S. industrial boiler capacity. Cast iron systems are generally used to burn oil or natural gas.[5] They are used to produce either low pressure steam or hot water. In a cast iron system combustion gases rise past a vertical heat exchanger. Water enters at the bottom of the heat exchanger, and rises through the exchanger tubes as it becomes heated. Cast iron systems are reliable and durable, with an average boiler life of about 50 years.[7] They require very little maintenance, and can handle overloading in demand surges. However, the cost of a cast iron boiler is generally higher than the cost of a firetube boiler of comparable size.

3.2.2.2 Firetube Boilers--

Firetube boilers make up about 24 percent of total U.S. industrial boiler capacity. These units generally are smaller than about 21 GJ/hr input capacity.[5] In firetube systems, combustion products pass through tubes submerged in water. Natural gas and oil are generally used as fuels, because the ash present in coal can cause tube fouling. Small units are generally fired by natural gas, while larger units are generally fired by distillate or residual oil. Firetube systems are used for space heating, process steam, and portable electric generation units.[5] They are susceptible to structural failure when subjected to large variations in steam demand, and are, therefore, used primarily where loads are relatively constant.

3.2.2.3 Watertube Boilers--

Watertube systems constitute about 69 percent of the total U.S. industrial boiler capacity. These systems range in input capacity from 0.42 to over 1580 GJ/hr. Package units are available with capacities up to about 256 GJ/hr; larger units are field-erected. In a watertube system, combustion gases contact the outsides of tubes into which water is fed to be converted to steam. The tubes are relatively small in diameter, and therefore provide rapid heat transfer, good response to steam demands, and high efficiency (≥ 80 percent). Also, because of the small tube diameter, watertube boilers can produce high pressure steam more safely than can firetube boilers. Boiler systems larger than about 53 GJ/hr and systems with steam pressures exceeding about 65 kPa are almost exclusively watertube systems. Watertube systems can burn any available fuel.

3.3 SIZE DISTRIBUTION AND AGE OF INDUSTRIAL BOILERS

Size distributions for the most widely used types of boilers in the industrial sector and for systems using different coal-firing techniques are presented in Table 5. This table also shows the total number and capacity of these combustion system categories. As shown in this table, cast iron systems with capacities less than 10 GJ/hr make up a large percentage (58 percent by number) of boilers used in the industrial sector; however, watertube systems in the 25 to 500 GJ/hr capacity range account for almost 70 percent of industrial boiler capacity. Firetube systems, in the 0.42 to 26.4 GJ/hr size range, account for an additional 13 percent of capacity. Coal-fired systems are, on the average, larger than gas or oil-fired systems; with pulverized coal-firing systems larger than 106 GJ/hr constituting 33 percent of the total coal-firing capacity, and spreader stokers, with a median capacity in the range of 106 to 265 GJ/hr, constituting another 23 percent. Table 6 shows the extent to which various atomization methods are used for different size ranges of oil-fired industrial boilers. Air atomization is the most common atomization technique for small units, while steam atomization is commonly used for larger systems.

There are approximately 1500 wood-fired industrial boilers in the United States. Table 7 shows the size distribution, by number, of wood-fired boilers sold between 1965 and 1973. Although the distribution presented in

TABLE 5. SIZE DISTRIBUTION OF INDUSTRIAL BOILERS

Boiler type	Percent (by number) in size range (GJ/hr)										Total number (1000)	Total capacity TJ/hr
	0-0.42	0.42-1.58	1.58-10.6	10.6-26.4	26.4-52.8	52.8-106	106-264	264-528	528-1580	>1580		
Natural gas												
Cast iron boiler	65.1	27.0	7.9								162	145
Firetube		59.8	8.2	1.5							88	400
Watertube		9.9	18.9	14.4	28.2	16.4	9.4	2.0	0.6	0.2	15	991
Distillate oil												
Cast iron boiler	68.0	23.9	8.1								38	24
Firetube	30.5	56.3	33.3	9.0	1.4						25	121
Watertube		29.9	38.5	9.9	13.3	4.1	3.7	0.5	0.1	0.02	5	92
Residual oil												
Cast iron boiler	68.0	23.9	8.1								60	39
Firetube		59.6	31.9	7.3	1.2						51	220
Watertube		6.5	20.6	17.0	30.5	13.9	8.7	2.2	0.5	0.01	12	634
Coal												
Cast iron boiler	63.0	26.0	11.0								36	23
Firetube	61.9	25.1	10.3	2.7							9	48
Watertube		2.9	8.7	9.5	29.8	21.8	20.1	5.5	1.4	0.3	6	584
Overfeed stoker		1.1	7.0	7.8	39.9	28.6	11.8	3.3	0.4	0.1	1	54
Underfeed stoker		5.2	13.6	13.5	35.3	25.6	5.5	1.1	0.2	0.03	3	160
Spreader stoker			3.4	6.6	27.6	21.0	34.9	5.6	0.7	0.2	1	154
Pulverized coal							63.0	26.6	8.9	1.5	1	216

Source: Reference 5.

TABLE 6. POPULATION DISTRIBUTION OF OIL-FIRED INDUSTRIAL BOILERS BY ATOMIZATION METHOD (1972)

	Percent by number in rated capacity range (GJ/hr)			
	10.6-17.5	17.5-106	106-264	264-528
Air atomization	40	15	5	1
Steam atomization	20	70	85	94
Mechanical atomization	10	10	10	5
Rotary cup atomization	30	5	--	--

Source: Reference 11.

TABLE 7. CAPACITY DISTRIBUTION OF WOOD-FIRED BOILER SALES FROM 1965 THROUGH 1973

Capacity range GJ/hr	Percent of boilers sold
8-13	2.2
13-79	72.8
79-197	18.4
197-394	3.3
Over 394	4.4

Source: Reference 11.

Table 7 is for a limited time period, it is expected to be typical of the capacity distribution of the total installed population. The distribution of firing designs in each capacity range is shown in Table 8 for wood-fired boilers sold between 1965 and 1976. It is clear from this table that spreader stokers are the most popular design, particularly in the larger sizes.

Data are available from boiler sales information on the age distribution of various types of industrial and commercial boilers that burn natural gas, oil, and coal.[5] These are presented in Table 9. As indicated in this table, over 95 percent of the coal-fired capacity in the industrial/commercial sector was over 10 years old in 1978. Also, coal-burning firetube systems have not been purchased in the past 10 years. The boiler age data for coal-fired units may indicate that a large number of units are on standby.[5]

3.4 CONTROL SYSTEM FOR INDUSTRIAL BOILERS

Data on emission control systems used for industrial boilers have been gathered using the National Emissions Data System (NEDS).[5,11] Natural gas and oil-fired systems generally are not controlled because they do not require controls to meet typical State Implementation Plan (SIP) regulations. Particulate emissions from coal-fired industrial boilers are generally controlled, while SO_2 emissions are generally not controlled. Table 10 presents the results of a survey of particulate emission control systems for a total of 2533 boilers.[12] The most frequently used control devices were various types of cyclones; uncontrolled boilers were also common.

Average collector efficiencies and total nationwide control efficiencies for coal-fired industrial boilers, based on NEDS data, are shown in Table 11. As this table shows, nearly all pulverized coal-fired systems and cyclone systems are equipped with control systems, while stoker systems are less frequently controlled. Typical SIPs require some degree of control (about 80 percent) for most coal-fired industrial boilers. Also, New Source Performance Standards promulgated in 1974 apply to all new, modified or reconstructed fossil fuel or wood-fired boilers with input capacities greater than 256 GJ/hr, and require approximately 99 percent control of particulate emissions for coal-fired systems in this size range.[13] New Source Performance

TABLE 8. DISTRIBUTION OF FIRING DESIGNS WITHIN CAPACITY RANGES IN WOOD-FIRED BOILER SALES, 1965-1975

	Percent (by number) in rated capacity range (GJ/hr)				
Firing design	8-13	13-79	79-197	197-394	Over 394
Spreader stoker	50.0	34.6	72.5	100.0	66.7
Underfeed stoker	0	1.9	0	0	0
Overfeed stoker	0	34.0	20.0	0	0
Suspension-firing	0	0	2.5	0	11.1
Other	50.0	29.5	5.0	0	22.2

Source: Reference 10.

TABLE 9. AGE DATA FOR INDUSTRIAL/COMMERCIAL SIZE BOILERS, 1978

System type	Percent of capacity <10 yrs old
Natural gas	
Cast iron	30
Firetube	27
Watertube	28
Distillate oil	
Cast iron	42
Firetube	37
Watertube	15
Residual oil	
Cast iron	43
Firetube	37
Watertube	20
Coal	
Cast iron	3
Firetube	0
Watertube	5

Source: Reference 5.

TABLE 10. CONTROL SYSTEMS USED FOR COAL-FIRED BOILERS

Control technique	Percent (by number)
No control	33
Cyclone	47
Scrubber	4
Electrostatic precipitator	14
Fabric filter	1

Source: Reference 12 (2533 units surveyed).

TABLE 11. ESTIMATED APPLICATION OF CONTROL EQUIPMENT TO COAL-FIRED INDUSTRIAL BOILERS, 1978

System type	Average collector efficiency (percent)	Control application (percent)	Net control (percent)
Pulverized	85	95	81
Cyclone	82	91	75
Stoker	85	62	53

Source: Reference 5 and 6.

Standards that would affect industrial boilers are expected to be proposed in the early 1980s.[14] Passage of these standards would result in increased application of control and installation of more efficient control systems, especially for particulate matter, in the future.

4.0 EMISSIONS

Flue gases represent the principal source of air emissions from industrial boilers. Pollutants emitted in flue gas streams include particulates, nitrogen oxides, sulfur oxides, sulfates, carbon monoxide, trace elements, and a variety of organic materials including polycyclic organic material (POM). Emissions of nitrogen oxides result from the oxidation of the nitrogen component of combustion air and nitrogen present in the fuel. Emissions of sulfur oxides, primarily SO_2, result from the oxidation of sulfur present in the fuel. The quantities of nitrogen oxides, SO_3, and sulfates emitted depend on the type of fuel burned, the amount of excess air present, and the flame temperature. The formation of SO_3 and sulfates is also catalyzed by trace elements in the fuel, such as vanadium and nickel.

Emissions of carbon monoxide and organic compounds such as hydrocarbons and POM result from incomplete combustion. Particulate matter emissions comprise combustion products of mineral compounds present in the fuel and products of incomplete combustion, such as soot. Elements present in the fuel are emitted primarily as particulates with some inorganic species emitted in gaseous form.

Fugitive air and water emissions from coal and ash storage piles in the industrial sector are relatively minor in comparison to such emissions from utility sources. Coal consumed by the industrial sector represents only about 10 percent of the coal burned by utilities; coal storage piles for industrial boilers are generally small, approximately 33 percent of the size of coal storage piles for a coal-fired utility boiler of similar capacity; and the average particulate collection efficiency of coal-fired industrial boilers is 70 percent compared to an overall collection efficiency of 92 percent for coal-fired utilities. Thus, fugitive air and water emissions from industrial coal and ash storage piles represent approximately 3.3 percent and 7.6

percent, respectively, of such emissions from the utility sector. These emissions have been examined in detail in the utility report (Volume III) of this EACCS program series and were not considered in this industrial combustion source sampling and analysis program. Fugitive emissions from gaseous and liquid fuels are considered minor because gaseous fuels are contained before combustion, and evaporation losses from liquid fuels are small because of their low volatility.

Other sources of air and water pollution and solid waste generation have also been examined in detail in the utility report and were not subjected to further examination in this study of industrial emissions. These sources include cooling towers, boiler blowdown and feedwater treatment, equipment cleaning, particulate scrubbers, and flue gas desulfurization (FGD) equipment. However, results of a detailed study of emissions from an industrial boiler burning either exclusively coal or oil and equipped with a double-alkali FGD unit, conducted under the auspices of this program, are described in Reference 15. Flue gas emissions from this unit are summarized in this report (site 200/201, pulverized coal and site 202/203, residual oil).

Because of the types and quantities of fuels burned, industrial combustion sources contribute more to the nationwide pollutant burden than commercial and residential combustion sources, but less than utility combustion sources. Industrial boilers are usually larger than residential and commercial sources, but are less numerous and better controlled. In general, industrial boilers have higher stacks, which promote dispersion of pollutants. Industrial boilers are smaller than utility boilers, but are generally not as well maintained and controlled. Poor maintenance can, in some instances, lead to excess emissions of potentially hazardous air pollutants, such as POM.

Detailed data on flue gas emissions from industrial boilers are presented in the following sections. As noted above, fugitive air emissions and pollutant emissions to water from industrial boilers are not discussed in this report. However, the trace element and organic content of a limited number of ash samples from wood burning sites were measured, and the data are discussed later in this section. Data, characterizing ash from wood combustion are limited and were felt to be of potential interest because of the high levels of POM compounds found in the flue gas of some wood-fired combustion sources.

4.1 EVALUATION OF EXISTING EMISSIONS DATA

4.1.1 Criteria for Evaluating the Adequacy of Emission Data

A major task in this program was the identification of gaps and inadequacies in the existing emissions data base for combustion sources. The results of this effort were used to determine the extent of the sampling and analysis program required to complete an adequate emissions assessment for each of the combustion source types. In addition, the data acquired during the sampling and analysis program, in combination with the existing data, also need to be assessed. Data inadequacies identified at the completion of the current program will require further study.

The criteria for assessing the adequacy of emissions data were developed by considering both the reliability and the variability of the data. A detailed presentation of the procedures used to identify and evaluate emissions data is given in Appendix A. Briefly, the general approach was to use a three-step process. In the first step, the available data were screened for adequate definition of process and fuel parameters that may affect emissions, as well as for validity and accuracy of sampling and analysis methods. In the second step of the data evaluation process, emissions data deemed acceptable in Step 1 were subjected to further engineering and statistical analyses to determine the internal consistency of the test results and the variability in emission factors. The third and final step in the process used a method developed by Monsanto Research Corporation (MRC) that is based on both the potential environmental risks associated with the emissions of each pollutant and the quality and variability of the data. The potential environmental risks associated with pollutant emissions were determined by using an ambient severity factor that is defined as the ratio of the calculated maximum ground-level concentration of the pollutant species for an isolated typical source to the level at which a potential environmental hazard exists. Data variability, V, is defined as

$$V = t \frac{s(\bar{x})}{\bar{x}}$$

where $s(\bar{x})$ is the standard deviation of the mean and $\bar{x}$ is the estimated mean value. Defined in this manner, data variability is a measure of the "relative precision" of the estimated mean emission factor, assuming a normal distribution of emission factors (see Appendix A). If the variability of emission factor data is < 70 percent, (equivalent to an accuracy factor of < 3, which has been defined by EPA as the acceptable accuracy for Level I sampling and analysis), the data are deemed adequate. However, if the variability of the emissions data is > 70 percent, the determination of data adequacy and the need for further measurement will be based on calculated ambient severity factors for each pollutant. The data will be considered adequate if the upper bound of the ambient severity factor is ≤ 0.05.

In addition to the general approach described above, fuel analysis, mass balance, and physico-chemical considerations can often be used to estimate emission levels and to establish the adequacy of the data base. For example, flue gas emissions of trace elements from oil-fired boilers can be determined from the trace element content of fuel oil by mass balance. Thus, an adequate characterization of the trace element content of fuel oil will provide an adequate characterization of trace element emissions from oil-fired boilers. Fuel sulfur content, ash content of coal, and the nitrogen content of residual oil are other examples of fuel characteristics that can be used to estimate emissions from combustion sources. EPA emission factors given in Reference 9 (AP-42) for particulates, sulfur oxides, and nitrogen oxides are dependent to varying degrees on certain of the above fuel characteristics. Certain combustion system characteristics; e.g., size, load, burner type, and other operational parameters, also affect emissions of some criteria pollutants. These effects are quantified in AP-42 for some combustion source categories.

Both fuel and combustion system characteristics are important factors affecting criteria pollutant emissions, and the magnitude of these factors can be determined for combustion source categories under representative combustion conditions by examination of EPA emission factors.[9] However, the existing emissions data base is too limited to allow estimation of criteria pollutant emissions under nonrepresentative or abnormal conditions of combustion source operation, nor is it possible to quantify emissions of certain pollutants, e.g., POM, under any conditions. Although emissions of POM are known to be dependent on such factors as fuel, burner efficiency, and load, the magnitude of such factors cannot be assessed given the present state of knowledge of emissions from combustion sources. A major objective of this program is to provide additional data for use in the assessment of the significance of POM and other emissions from representative combustion source categories, using the general approach described previously.

4.1.2 Existing Emissions Data: Gas-Fired Sources

4.1.2.1 Criteria Pollutant Emissions--

Criteria pollutant emissions data for gas-fired industrial-size boilers have been obtained by KVB Engineering, Inc.[16,17] These data were obtained under several different operating conditions for representative gas-fired units, including 23 watertube boilers and nine firetube boilers. Input capacities of these units ranged from 8.5 to 338 GJ/hr. A summary of the criteria pollutant emissions data obtained at baseline conditions (approximately 80 percent load and 10 percent CO_2) is presented in Table 12. For each pollutant, this table shows the number of data points, the mean emission factor, the variability of the mean, the ambient source severity factor, an assessment of the data base adequacy, and for comparison, the published EPA emission factor.[9] Detailed test results are presented in Appendix C with information on the units tested, including age, efficiency, and stack gas composition.

As indicated in Table 12, the data base for criteria pollutant emissions from gas-fired industrial boilers is considered adequate. The variability of hydrocarbon emissions data exceeds 70 percent; however, the upper limit of the severity factor for this pollutant is below 0.05. The only criteria pollutant of potential environmental significance for gas-fired industrial boilers is NO_x, with a mean severity factor exceeding 0.1. However, emission factors shown in Table 12 for hydrocarbons, CO, and SO_2 are higher than published EPA emission factors by 5- to 10-fold. In the cases of hydrocarbons and CO, the discrepancies are probably attributable to boiler operating conditions. The discrepancy in the case of SO_2 can not be attributed to boiler operating conditions, because SO_2 emissions from natural gas firing depend only on the fuel sulfur content. Because the published EPA emission factor for SO_2 was calculated from fuel sulfur content, the KVB data are suspect.

TABLE 12. SUMMARY OF CRITERIA POLLUTANT EMISSIONS DATA FOR GAS-FIRED INDUSTRIAL BOILERS

Pollutant	Number of data points	Mean emission factor (ng/J)	Variability (percent)	Ambient severity factor[a]	Data base adequacy[b]	EPA emission factor (ng/J)
Particulate	14	2.46	24	0.0012	A	2.10-6.29
SO_2	2	3.20	-	0.0011	A	0.3
NO_x (as NO_2)	36	71.4	20	0.1160	A	50.30-96.50
Hydrocarbons	22	6.81	71	0.0134[c]	A	1.26
CO	36	32.8	65	0.0002	A	7.13

[a] Based on a firing rate of 13.5 GJ/hr and a stack height of 23 meters.

[b] Adequate data base is indicated by A.

[c] Upper limit of severity factor.

4.1.2.2 Fine Particulate Emissions--

KVB Engineering, Inc., also attempted to determine the particle size distribution of fly ash from six gas-fired industrial boilers by optical classification.[16] The results of the KVB study are variable: for three boilers the majority of particles emitted were larger than 6μm, whereas for the other three, the majority of particles were smaller than 6 μm. Also, the relative numbers of small particles (< 2μm) were not determined in five of the six tests because of the difficulty in counting small particles by the optical technique used. However, the lack of particle size distribution data does not represent a serious data deficiency, because of the relatively low particulate emissions from gas-fired sources.

4.1.2.3 Sulfate and Trace Element Emissions--

Sulfate and trace element emissions data were not found in the literature for natural gas-fired industrial sources. However, because of the low sulfur and trace element contents of natural gas, the lack of data does not represent a serious deficiency.

4.1.2.4 Specific Organic and POM Emissions--

Emissions of POM from a gas-fired process heating boiler were measured by the Public Health Service.[18] The unit tested was a firetube boiler with a rated capacity of 7.6 GJ/hr. During testing the unit was operated at a firing rate of about 9.8 GJ/hr. Test samples were obtained by passing the flue gas through two water impingers at 0°C, a series of freeze-out traps at -17°C, and a high efficiency filter. Organic material was then extracted from the samples with benzene and separated into a number of fractions by chromatography, and concentrations of specific compounds were measured by ultraviolet-visible spectroscopy. Table 13 presents the results of these measurements. Because POM data are available for only one gas-fired boiler, no meaningful measure of variability or ambient severity is possible.

TABLE 13. POM EMISSIONS FROM A GAS-FIRED INDUSTRIAL BOILER[18]

Pollutant	Emissions (pg/J)
Total benzene soluble organics	1040
Benzo (a) pyrene	0.2
Pyrene	0.004
Benzo (e) pyrene	0.014
Perylene	ND
Benzo (g,h,i) pyrene	ND
Anthanthrene	ND
Coronene	0.012
Anthracene	ND
Phenanthrene	ND
Fluoranthrene	0.09

ND -- not detected.

Generally, emissions of POM from gas-fired sources are not of concern because of the chemical makeup of natural gas. Natural gas contains predominantly saturated hydrocarbons, which do not promote the addition reactions between hydrocarbon species necessary to form large molecular weight hydrocarbons. Also, cyclic compounds, which form convenient building blocks for POMs, are not generally present in natural gas. However, because of the severity of POM exposure and the deficiency of data, further testing for POM emissions from gas-fired boilers was conducted.

4.1.3 Existing Emissions Data: Oil-Fired Sources

4.1.3.1 Criteria Pollutant Emissions--

KVB and Environmental Ultrasystems obtained criteria pollutant emissions data for a number of distillate and residual oil-fired industrial size boilers at a variety of operating conditions.[16,17,19,20] Emissions data were obtained at baseline conditions (approximately 80 percent load and 12 percent CO_2) for 14 distillate oil-fired boilers and 24 residual oil-fired boilers. These boilers include firetube systems using air and steam atomization; and watertube systems using air, steam, and mechanical atomization. The distillate oil-fired boilers tested ranged in input capacity from about 4 to 145 GJ/hr; the residual oil-fired units ranged from about 4 to 660 GJ/hr input capacity. The results of tests conducted at baseline conditions are presented in Appendix C and summarized for distillate and residual oil-fired sources in Tables 14 and 15, respectively. Appendix C presents information on the units tested, including ages and efficiencies, as well as information on operating conditions and fuel sulfur contents. Tables 14 and 15 present mean emission factors, emission factor variabilities, and ambient severity factors for criteria pollutant emissions from distillate and residual oil-fired sources, respectively. The tables also present assessments of data base adequacy and, for comparison, published EPA emission factors.[9]

As shown in Table 14 and 15, the criteria pollutant emissions data base for distillate and residual oil-fired industrial boilers are considered adequate. Emission factor variabilities for hydrocarbons and CO from distillate oil-fired boilers and hydrocarbons from residual oil-fired boilers are greater than 70 percent; however, the upper limit ambient severity factors for these pollutants are all much less than 0.05. Emissions of NO_x from both distillate and residual oil-fired boilers and SO_2 from residual oil-fired boilers are environmentally significant, with ambient severity factors exceeding 0.05. Also, ambient severity factors for SO_2 emissions from distillate oil-fired units and particulate emissions from residual oil-fired units approach 0.05 -- 0.022 and 0.020, respectively.

TABLE 14. SUMMARY OF CRITERIA POLLUTANT EMISSIONS DATA FOR DISTILLATE OIL-FIRED INDUSTRIAL BOILERS

Pollutant	Number of data points	Mean emission factor (ng/J)	Variability (percent)	Ambient severity factor[a]	Data base adequacy[b]	EPA emission factor (ng/J)
Particulate	9	13.7	31	0.0036	A	6.41
SO_2	9	494S[c]	29	0.0221[d]	A	455S[c]
NO_x (as NO_2)	20	66.2	14	0.0568	A	70.6
Hydrocarbons	5	1.86	135	0.0026[e]	A	3.21
CO	18	2.06	98	<0.0001[e]	A	16.0

[a] Based on a firing rate of 7.1 GJ/hr and a stack height of 23 meters.

[b] Adequate data base is indicated by A.

[c] S refers to the percentage of sulfur by weight in the oil.

[d] Based on a average fuel sulfur content of 0.24 percent.

[e] Upper limit of severity factor.

TABLE 15. SUMMARY OF CRITERIA POLLUTANT EMISSIONS DATA FOR RESIDUAL OIL-FIRED INDUSTRIAL BOILERS

Pollutant	Number of data points	Mean emission factor (ng/J)	Variability (percent)	Ambient severity factor[a]	Data base adequacy[b]	EPA emission factor (ng/J)
Particulate	22	39.3	35	0.0200	A	30.
SO_2	25	435S[c]	9	0.1590[d]	A	462S
NO_x (as NO_2)	34	151	12	0.2460	A	177
Hydrocarbons	13	3.02	75	0.0061[e]	A	2.94
CO	31	3.72	61	<0.0001	A	14.7

[a] Based on a firing rate of 13.5 GJ/hr and a stack height of 23 meters.

[b] Adequate data base is indicated by A.

[c] S refers to the percentage of sulfur in the oil.

[d] Based on an average fuel sulfur content of about 1.03 percent.

[e] Upper limit severity factor.

4.1.3.2 Fine Particulate Emissions--

Particle size distribution data by mass were obtained by KVB Engineering, Inc., for two distillate oil-fired industrial boilers and six residual oil-fired boilers.[17,19] These data are summarized in Table 16. Mass median diameters ranged from 3.4 to 5.0 μm for distillate oil-fired boilers and from less than 1.0 μm to 3.4 μm for residual oil-fired boilers. Percentages of respirable particles (particles less than about 3 μm) ranged from 26 to 55 percent for distillate oil-fired sources, and from 46 to 93 percent for residual oil-fired sources. The particle size data base for residual oil-fired systems is adequate; however, the data base for distillate oil-fired systems must be considered inadequate.

4.1.3.3 SO_3 and Sulfate Emissions--

Data obtained by KVB indicate that the ratio of SO_3 emissions to SO_x emissions from oil-fired industrial boilers is typically 1 to 2 percent.[17,19] The data show a sharp increase in this ratio at low SO_2 emission rates; however, this effect was attributed by KVB to inadequacies in the SO_3 measurement technique at low concentrations.[17] The rate of formation of SO_3 is generally directly proportional to the concentration of SO_2. Formation of SO_3 is also enhanced by increased combustion oxygen and by the presence of trace elements such as vanadium and nickel, which catalyze the conversion of SO_2 to SO_3. No data are available on the conversion of SO_3 to primary sulfate in industrial boilers.

Using the SO_x emission rates presented in Tables 14 and 15, if 1.5 percent of the sulfur emitted from oil-fired industrial boilers is emitted as SO_3, emission factors for SO_3 from distillate and residual oil-fired boilers are 1.8 ng/J and 6.7 ng/J, respectively. Ambient severity factors for these emission rates are 0.067 and 0.26, respectively. Based on these factors, SO_3 emissions from both distillate and residual oil-fired industrial boilers are significant.

TABLE 16. PARTICLE SIZE DISTRIBUTION DATA FOR OIL-FIRED INDUSTRIAL BOILERS

System description	Average particulate emissions	Mass median diameter[a]	Fraction by weight in size range		
			<1 µm[a]	<3 µm[a]	<10 µm[a]
Distillate oil-fired					
Mean	15.5 ng/J	4.2 µm	0.13	0.40	0.79
Variability	----	----	----	----	----
Range	6.88-24.2 ng/J	3.4-5.0 µm	0.03-0.23	0.26-0.55	0.75-0.83
Residual oil-fired					
Mean	56.5 ng/J	2.0 µm	0.48	0.64	0.89
Variability	133%	65%	56%	32%	6.6%
Range	26.2-127 ng/J	1.0-3.4 µm	0.15-0.86	0.46-0.93	0.85-0.97

[a] Diameters are aerodynamic.

4.1.3.4 Trace Element Emissions--

The trace element data base for residual oil-fired industrial boilers is limited to data obtained by KVB for a residual oil-fired boiler.[19] However, for oil combustion, emissions of trace elements can be estimated with a good degree of accuracy by assuming that all trace elements present in oil are emitted in the flue gas. Table 17 presents average trace element contents of residual oil, based on a weighted average of residual oils used in the United States.[21] Emission factors and mean ambient source severity factors calculated using these data are presented in Table 18. Emissions of several elements have severity factors greater than 0.05, and are therefore of environmental concern. Elements for which mean source severities exceed 0.05 are arsenic, beryllium, cadmium, cobalt, chromium, iron, potassium, nickel, lead, uranium, and vanadium. Because no data are available on the variability of trace element concentrations in residual oil, and because emissions of several trace elements from industrial residual oil-fired boilers appear to be environmentally significant, the data base for trace element emissions from industrial residual oil-fired boilers is considered inadequate.

Data on trace element concentrations in distillate oil or on trace element emissions from distillate oil combustion were not found in the literature. However, emissions of trace elements from distillate oil combustion are generally much lower than emissions from residual oil combustion.

4.1.3.5 Specific Organic and POM Emissions--

Emissions of POM from oil-fired industrial boilers have been measured by the Public Health Service and by KVB Engineering.[18,19] In the Public Health Service tests, samples were collected by passing the flue gas through two water impingers at 0°C, a series of freeze-out traps at -17°C, and a high efficiency filter. Organic matter was extracted from the filter catch with benzene and separated into fractions using chromatography. Concentrations of specific compounds were measured by ultraviolet-visible spectroscopy.[18] In the KVB tests, samples were collected by passing the flue gas through XAD-2 resin, and concentrations of specific organics were determined using combined gas chromatography/mass spectroscopy.[19]

TABLE 17. AVERAGE TRACE ELEMENT CONCENTRATIONS OF RESIDUAL OIL

Trace element	Concentration, ppm	Trace element	Concentration, ppm
Vanadium	160	Gallium	0.4
Nickel	42.2	Indium	0.3
Potassium	34	Silver	0.3
Sodium	31	Germanium	0.2
Iron	18	Thallium	0.2
Silicon	17.5	Zirconium	0.2
Calcium	14	Strontium	0.15
Magnesium	13	Bromine	0.13
Chlorine	12	Fluorine	0.12
Tin	6.2	Ruthenium	0.10
Aluminum	3.8	Tellurium	0.1
Lead	3.5	Cesium	0.09
Copper	2.8	Beryllium	0.08
Cadmium	2.27	Iodine	0.06
Cobalt	2.21	Lithium	0.06
Rubidium	2	Mercury	0.04
Titanium	1.8	Tantalum	0.04
Manganese	1.33	Rhodium	0.03
Chromium	1.3	Gold	0.02
Barium	1.26	Platinum	0.02
Zinc	1.26	Scandium	0.02
Phosphorus	1.1	Bismuth	0.01
Molybdenum	0.90	Cerium	0.006
Arsenic	0.8	Tungsten	0.004
Selenium	0.7	Hafnium	0.003
Uranium	0.7	Yttrium	0.002
Antimony	0.44	Niobium	0.001
Boron	0.41		

Source: Reference 21.

TABLE 18. TRACE ELEMENT EMISSION FACTORS AND MEAN AMBIENT SEVERITY FACTORS FOR RESIDUAL OIL-FIRED INDUSTRIAL BOILERS

Trace element	Concentration (ppm)	Emission factor (pg/J)	Ambient[a] severity factor
Aluminum (Al)	3.8	87	0.002
Arsenic (As)	0.8	18	1.1
Boron (B)	0.41	9.4	<0.001
Barium (Ba)	1.26	28.8	0.008
Beryllium (Be)	0.08	1.8	0.11
Bromine (Br)	0.13	3.0	<0.001
Calcium (Ca)	14	320	0.002
Cadmium (Cd)	2.27	51.9	0.64
Chlorine (Cl)	12	274	0.012
Cobalt (Co)	2.21	50.5	0.12
Chromium (Cr)	1.3	30	2.7
Copper (Cu)	2.8	64	0.638
Fluorine (F)	0.12	2.7	<0.001
Iron (Fe)	18	411	0.05
Mercury (Hg)	0.04	0.9	0.002
Potassium (K)	34	777	0.48
Lithium (Li)	0.06	1.4	0.006
Magnesium (Mg)	13	297	0.006
Manganese (Mn)	1.33	30.4	<0.001
Molybdenum (Mo)	0.9	21	<0.081
Sodium (Na)	31	708	0.034
Nickel (Ni)	42.2	964	7.8
Phosphorus (P)	1.1	25	0.004
Lead (Pb)	3.5	80	0.066
Antimony (Sb)	0.44	10	0.002
Selenium (Se)	0.7	16	0.010
Silicon (Si)	17.5	400	0.004
Tin (Sn)	6.2	142	0.004
Strontium (Sr)	0.15	3.4	<0.001
Thorium (Th)	<0.001	0.02	<0.001
Uranium (U)	0.7	16	0.22
Vanadium (V)	160	3656	0.90
Zinc (Zn)	1.26	28.8	<0.001

[a] Based on a firing rate of 50 x 10^9 J/hr.

The results of these tests are presented in Table 19. Because of difficulties in sample analysis, the results of the KVB tests (unit 3) show only the lower limits of POM emissions. Variabilities and severity factors for the Public Health Service data were not calculated because of the limited number of tests and the variations in fuel used and boiler load. The data base for POM emissions from distillate and residual oil-fired industrial boilers must be considered inadequate.

TABLE 19. POM EMISSIONS FROM OIL-FIRED INDUSTRIAL BOILERS, pg/J

Pollutant	Combustion sources, firing rates, and fuels		
	Unit 1 22 GJ/hr #2 oil[a]	Unit 2 15 GJ/hr #6 oil[b]	Unit 3 20 GJ/hr #6 oil[c]
Total benzene soluble organics	1320	3130	>0.009
Benzo (a) pyrene	<0.02	0.05	>0.000007
Pyrene	0.04	0.3	>0.00009
Benzo (e) pyrene	ND	ND	>0.000007
Perylene	ND	ND	NM
Benzo (g,h,i) pyrene	ND	ND	NM
Anthanthrene	ND	ND	NM
Coronene	ND	ND	NM
Anthracene	ND	ND	>0.0056
Phenanthrene	ND	1.8	ND
Fluoranthrene	0.05	0.3	>0.0021
Methyl anthracenes	NM	NM	>0.00037
Dibenz (a,h) anthracene	NM	NM	ND
Benzo (c) phenanthrene	NM	NM	0.000005
3-Methylcholanthrene	NM	NM	ND
Dibenzo (a,h) pyrene	NM	NM	ND
Dibenzo (a,i) pyrene	NM	NM	ND
Dibenzo (c,g) carbazole	NM	NM	ND
Chrysene	NM	NM	>0.000044
Benzofluoranthrenes	NM	NM	>0.00001

ND -- not detected
NM -- not measured

[a] Reference 18. Steam atomized watertube unit operating at 91 percent load.

[b] Reference 18. Steam atomized watertube unit operating at 48 percent load.

[c] Reference 19. Mechanical atomization watertube unit operating at 83 percent load. Because of difficulties in sample analysis, emissions data reported for this unit show only the lower limits of POM emissions.

4.1.4 Existing Emissions Data: Coal-Fired Sources

4.1.4.1 Criteria Pollutant Emissions--

Bituminous Coal-Fired Sources--KVB Engineering obtained criteria pollutant emissions data for bituminous coal-fired industrial boilers operating under a variety of conditions.[16,17,22-24,26] The sources tested include nine pulverized coal-fired boilers ranging in input capacity from 132 GJ/hr to 1500 GJ/hr, 11 spreader stokers with capacities ranging from 66 GJ/hr to 417 GJ/hr input capacity, and 13 grate type and underfeed stokers with input capacities ranging from 13 GJ/hr to 80 GJ/hr. All of these systems used watertube boilers. The results of tests conducted at baseline conditions (approximately 80 percent load and 10 percent CO_2) are presented in Appendix C with information on operating conditions, stack gas concentrations, and fuel sulfur and ash contents. Summaries of particulate, SO_2, NO_x, hydrocarbon, and CO emissions data are presented in Tables 20 through 24, respectively. For each of the above boiler types, the tables present the number of data points, the average emission factor, the variability and the ambient severity factor associated with the emission factor, an assessment of the data base adequacy, and, for comparison, the published EPA emission factor.[9]

Because data were available for only one cyclone system, the criteria pollutant emissions data base for cyclones must be considered inadequate. However, as noted in Chapter 3 (Table 3), cyclone systems consume only about 2.6 percent of the coal used as fuel in the industrial sector.

Particulate emission factors and associated ambient severity factors are presented in Table 20 for both controlled and uncontrolled emissions. Controlled emissions were determined using the average particulate control efficiencies shown in Section 3 (Table 11) for the various boiler types. Although the emission factors for pulverized dry bottom systems and other stokers are roughly a factor of two lower than their respective EPA emission factors, the variability of the data is less than 70 percent and the data are adequate for these units. Data variability is greater than 70 percent for spreader stokers and therefore the data base is inadequate. Because only one cyclone was tested the data base for cyclones is also inadequate. Ambient severity factors exceed 0.05 for all combustion systems, including the controlled systems. Control systems with efficiencies greater than 95 percent would be required to reduce ambient severity factors to 0.05 or less.

For pulverized coal-fired systems and stokers, the data base for SO_2 emissions is considered adequate. The emission factors for SO_2 have variabilities well under 70 percent and, when the variabilities are taken into account, are in agreement with published EPA emission factors. SO_2 emissions are environmentally significant for all of the coal combustion systems studied.

TABLE 20. SUMMARY OF PARTICULATE EMISSIONS DATA FOR BITUMINOUS COAL-FIRED INDUSTRIAL BOILERS

Combustion system	Number of data points	Mean emission factor (ng/J)		Variability (percent)	Ambient severity factor[b]		Data base adequacy	EPA emission factor (ng/J)
		Uncontrolled	Controlled[a]		Uncontrolled	Controlled		
Pulverized, dry	6	148[d]	22A[d]	27	3.2	0.49	A	332A[d]
Cyclone	1	68A[d]	12A[d]	--	1.5	0.27	I	39A[d]
Spreader stoker	25	331A[d]	50A[d]	83	10.[e]	1.5[e]	I	254A[d]
Other stoker	15	59A[d]	9A[d]	63	1.5	0.23	A	98A[d]

[a] Efficiencies of control used to calculate controlled emissions are 85 percent for pulverized coal-fired boilers and stokers, and 82 percent for cyclones (Chapter 3, section 3.3).

[b] Based on heat capacities of 200 GJ/hr for pulverized coal-fired boilers and cyclones, 150 GJ/hr for spreader stokers, and 50 GJ/hr for other stokers; stack heights of 50 meters for pulverized coal-fired boilers, cyclones, and spreader stokers, and 23.2 meters for other stokers; and an average ash content for bituminous coal of 14.09 percent.

[c] Adequate data base is indicated by A and inadequate data based is indicated by I.

[d] A indicates fuel ash content in percent.

[e] Upper limit severity factor.

TABLE 21. SUMMARY OF SO_2 EMISSIONS DATA FOR BITUMINOUS COAL-FIRED INDUSTRIAL BOILERS

Combustion system	Number of data points	Mean emission factor (ng/J)	Variability (percent)	Ambient severity factor[a]	Data base adequacy[b]	EPA emission factor (ng/J)
Pulverized, dry	6	619S[c]	25	1.3	A	743S[c]
Cyclone	1	325S[c]	--	0.69	I	743S[c]
Spreader stoker	22	758S[c]	10	1.2	A	743S[c]
Other stoker	10	688S[c]	12	1.7	A	743S[c]

[a] Based on heat capacities of 200 GJ/hr for pulverized coal-fired boilers and cyclones, 150 GJ/hr for spreader stokers, and 50 GJ/hr for other stokers; stack heights of 50 meters for pulverized coal-fired boilers, cyclones, and spreader stokers, and 23.2 meters for other stokers; and on an average fuel sulfur content of 1.92 percent.

[b] Adequate data based is indicated by A and inadequate data base is indicated by I.

[c] S indicates percent sulfur in fuel.

TABLE 22. SUMMARY OF NO_x EMISSIONS DATA FOR BITUMINOUS COAL-FIRED INDUSTRIAL BOILERS

Combustion system	Number of data points	Mean emission factor (ng/J)	Variability (percent)	Ambient severity factor[a]	Data base adequacy[b]	EPA emission factor (ng/J)
Pulverized, dry	6	243	30	1.7	A	352
Cyclone	1	482	--	3.4	I	1070
Spreader stoker	25	238	7	1.2	A	293
Other stoker	15	127	16	1.0	A	293

[a] Based on heat capacities of 200 GJ/hr for pulverized coal-fired boilers and cyclones, 150 GJ/hr for spreader stokers, and 50 GJ/hr for other stokers; stack heights of 50 meters for pulverized coal fired boilers, cyclones, and spreader stokers, and 23.2 meters for other stokers.

[b] Adequate data base is indicated by A and inadequate data base is indicated by I.

TABLE 23. SUMMARY OF HYDROCARBON EMISSIONS DATA FOR BITUMINOUS COAL-FIRED INDUSTRIAL BOILERS

Combustion system	Number of data points	Mean emission factor (ng/J)	Variability (percent)	Ambient severity factor[a]	Data base adequacy[b]	EPA emission factor (ng/J)
Pulverized, dry	5	3.3	111	0.025[c]	A	6
Cyclone	--	--	--	--	I	6
Spreader stoker	3	4.0	80	0.019[c]	A	6
Other stoker	--	--	--	--	--	6

---

[a] Based on heat capacities of 200 GJ/hr for pulverized coal-fired boilers and cyclones, 150 GJ/hr for spreader stokers, and 50 GJ/hr for other stokers; stack heights of 50 meters for pulverized coal fired boilers, cyclones, and spreader stokers, and 23.2 meters for other stokers.

[b] Adequate data base is indicated by A and inadequate data base is indicated by I.

[c] Upper limit of severity factor.

TABLE 24. SUMMARY OF CO EMISSIONS DATA FOR BITUMINOUS COAL-FIRED INDUSTRIAL BOILERS

Combustion system	Number of data points	Mean emission factor (ng/J)	Variability (percent)	Ambient severity factor[a]	Data base adequacy[b]	EPA emission factor (ng/J)
Pulverized, dry	4	0	0	0	A	20
Cyclone	1	0	--	0	I	20
Spreader stoker	30	132	47	0.0017	A	20
Other stoker	14	250	76	0.0089[c]	A	20

---

[a] Based on heat capacities of 200 GJ/hr for pulverized coal-fired boilers and cyclones, 150 GJ/hr for spreader stokers, and 50 GJ/hr for other stokers; stack heights of 50 meters for pulverized coal fired boilers, cyclones, and spreader stokers, and 23.2 meters for other stokers.

[b] Adequate data base is indicated by A and inadequate data base is indicated by I.

[c] Upper limit of severity factor.

The NO_x emissions data base for pulverized coal-fired systems and stokers is considered adequate, based on the data variability. The NO_x emission factor for small stokers is lower by a factor of about 2.3 than the published EPA emission factor; however the EPA emission factor is based on a compilation of data for all stokers, including spreader stokers. NO_x emissions from all of the coal combustion systems considered are associated with ambient severity factors greater than 1, and are therefore considered environmentally significant.

Although hydrocarbon and CO emission factors derived from the literature have high variabilities and are not generally in agreement with published EPA emission factors, the ambient severity factors associated with these emission factors are well below 0.05. Therefore the data base for hydrocarbon and CO emissions from pulverized coal-fired systems and stokers is considered adequate. No data are available on hydrocarbon emissions from small stokers; however, hydrocarbon emissions from these stokers are expected to be similar to hydrocarbon emissions from spreader stokers.

Anthracite and Lignite Coal-Fired Sources--Data were not available in the literature on criteria pollutant emissions from anthracite and lignite coal-fired sources. However, anthracite and lignite coals account for only about 0.65 percent and 2.6 percent, respectively, of the coal used for fuel in the industrial sector. Published EPA emission factors for criteria pollutants from anthracite and lignite coal-fired sources and associated severity factors are presented in Table 25.[9] Controlled particulate emission factors and associated severity factors are also presented, based on an average particulate emission control efficiency for stokers of 85 percent (Table 11).

Mean ambient severity factors for SO_2 emissions, NO_x emissions, and uncontrolled particulate emissions are in excess of 0.05 for both anthracite and lignite coal-fired sources. Also, severity factors of controlled particulate emissions and hydrocarbon emissions from lignite coal-fired sources exceed 0.05, and the severity factor for controlled particulate emissions from anthracite coal-fired sources approaches 0.05. Average severity factors for CO emissions from both anthracite and lignite coal-fired sources, and hydrocarbon emissions from anthracite coal-fired sources, are well below 0.05; therefore these emissions are not considered environmentally significant. However, because no data are available to determine the variability of emissions from anthracite and lignite coal-fired sources, the data base for all criteria pollutant emissions from these sources must be considered inadequate.

TABLE 25. PUBLISHED EPA EMISSIONS FACTORS AND AMBIENT SOURCE SEVERITY FACTORS FOR ANTHRACITE- AND LIGNITE-FIRED BOILERS

	Anthracite-fired boilers[a]		Lignite-fired boilers[b]	
Pollutant	Emission factor (ng/J)	Ambient severity factor[c]	Emission factor (ng/J)	Ambient severity factor[c]
Particulate --				
Uncontrolled	14A[d]	0.25	225A[d]	1.1
Controlled	2A[d]	0.037	34A[d]	0.16
SO_2	551S[e]	0.41	966S[e]	0.45
NO_x	145	1.2	193	1.0
Hydrocarbon	0	0	32.2	0.087
CO	14.5	0.0002	64.4	0.0008

[a] All stokers.

[b] Spreader stokers.

[c] Based on heat capacities of 150 GJ/hr for lignite-fired spreader stokers and 50 GJ/hr for anthracite-fired stokers; stack heights of 50 meters for lignite-fired spreader stokers and 23.2 meters for anthracite-fired stokers; and the following fuel sulfur and ash contents: anthracite coal -- A = 10 percent, S = 0.57 percent; and lignite coal -- A = 7.13 percent, S = 0.65 percent.

[d] A indicates percent ash in fuel.

[e] S indicates percent sulfur in fuel.

4.1.4.2 Fine Particulate Emissions--

Particle size data for uncontrolled emissions from bituminous coal-fired industrial boilers are available from two sources. Data on a pulverized coal-fired system were acquired by Monsanto,[25] and data for pulverized systems, spreader stokers, and other stokers were acquired by KVB Engineering.[17,23,24,26] These data are summarized in Table 26. For each of the various combustion systems, average values, variabilities, and ranges are presented for the mass fractions of particles smaller than 1 μm, 3 μm, and 10 μm.

TABLE 26. SUMMARY OF PARTICLE SIZE DATA FOR UNCONTROLLED EMISSIONS FROM BITUMINOUS COAL-FIRED BOILERS

	Fraction of particulate in aerodynamic size range		
	<1 μm	<3 μm	<10 μm
Pulverized, dry			
Average (3 tests)	0.04	0.19	0.40
Variability	155%	131%	124%
Range	0.013-0.08	0.12-0.3	0.17-0.54
Spreader stoker			
Average (8 tests)	0.02	0.08	0.17
Variability	97%	117%	76%
Range	0.011-0.08	0.025-0.35	0.08-0.48
Other stoker			
Average (6 tests)	0.23	0.32	0.40
Variability	85%	54%	39%
Range	0.10-0.58	0.21-0.64	0.28-0.68

Data are also available on the average collection efficiencies of different control devices for particles in various size ranges. Collection efficiencies for particles in the <1 μm, 1-3 μm, 3-10 μm, and >10 μm aerodynamic size ranges are presented in Table 27 for a medium efficiency cyclone, a multiclone, a medium efficiency scrubber, an electrostatic precipitator, a venturi scrubber, and a fabric filter.

Mass emission rates of particles smaller than 1 μm, 3 μm, and 10 μm are presented in Table 28 for pulverized coal-fired systems, spreader stokers, and other stokers equipped with the control devices listed above. Total uncontrolled particulate loadings were taken from Table 20; uncontrolled emission factors for different size ranges were calculated using these loadings and the particle size data presented in Table 26. Controlled emission factors were then calculated using the uncontrolled emission factors for the various size ranges and the control efficiencies presented in Table 27.

TABLE 27. EFFICIENCIES OF PARTICULATE REMOVAL BY CONTROL DEVICES FOR VARIOUS SIZE FRACTIONS

Particulate control device	Percent efficiencies of particulate removal for various aerodynamic size ranges			
	<1 μm	1-3 μm	3-10 μm	>10 μm
Medium efficiency cyclone	0.25	12	50	70
Multiclone	11	54	85	95
Medium efficiency scrubber	26	77	98.0	99.6
High efficiency ESP	96.5	98.25	99.1	99.5
Venturi scrubber	71	99.5	>99.8	>99.8
Fabric filter	96	99.75	>99.95	>99.95

Source: Reference 27

TABLE 28. ESTIMATED UNCONTROLLED AND CONTROLLED FINE PARTICULATE EMISSIONS FROM BITUMINOUS COAL-FIRED BOILERS

Combustion system and emission control technique	Emission factors for aerodynamic particle size ranges (ng/J)			
	<1 μm	<3 μm	<10 μm	Total
Pulverized, dry				
Uncontrolled	75.1	390	838	2085
Medium efficiency cyclone	74.9	352	576	950
Multiclone	66.8	212	279	341
Medium efficiency scrubber	55.5	128	137	142
High efficiency ESP	2.63	8.14	12.2	18.4
Venturi scrubber	21.8	23.4	23.4-24.2	23.4-26.7
Fabric filter	3.00	3.79	3.79-4.01	3.79-4.63
Spreader stoker				
Uncontrolled	97.9	368	769	4664
Medium efficiency cyclone	97.7	336	537	1705
Multiclone	87.2	222	282	477
Medium efficiency scrubber	72.5	149	157	235
High efficiency ESP	3.43	8.16	11.8	46.8
Venturi scrubber	28.4	29.8	29.8-30.6	29.8-38.4
Fabric filter	3.92	4.60	4.60-4.80	4.60-6.75
Other stoker				
Uncontrolled	191	266	332	831
Medium efficiency cyclone	191	257	290	440
Multiclone	170	204	214	239
Medium efficiency scrubber	141	158	159	161
High efficiency ESP	6.69	8.00	8.60	11.1
Venturi scrubber	55.4	55.8	55.8-55.9	55.8-56.9
Fabric filter	7.65	7.84	7.84-7.87	7.84-8.12

As shown in Table 26, variabilities for the percentages of particles in various size ranges for different boiler types are generally high. Only the variabilities of the percentages of particles smaller than 10 μm and smaller than 3 μm for stokers, other than spreader stokers, are lower than 0.70. In addition, the variability of mass emission rates for a particular size range would be approximately equal to the sum of the variability of the total uncontrolled particulate emission rate for the boiler type under consideration, the variability of the percentage of particles in the given size range for that boiler type, and, if controlled emissions are under consideration, the variability of the control efficiency for the given size range. For this reason, the mass emission rate of particles in a given size fraction cannot be calculated with a good degree of reliability.

Thus, the data base for fine particulate emissions from bituminous coal-fired boilers must be considered inadequate. No data were found in the literature for the particle size distributions of emissions from anthracite or lignite coal-fired boilers.

4.1.4.3 SO_3 and Sulfate Emissions--

The data base for SO_3 and sulfate emissions from coal-fired industrial boilers is limited. Sulfur trioxide emissions were measured by KVB for a pulverized coal-fired unit and two stokers, and by Monsanto Research Corporation for another pulverized coal-fired unit.[17,23,25] These data are summarized in Table 29. As shown in this table, the average fraction of fuel sulfur converted to SO_3 during the above tests was 0.81 percent, and the variability of this fraction is 174 percent. There are insufficient data to determine whether SO_3 emission rates vary for different combustion systems or for different operating parameters. Also, no data are available on SO_3 emission from anthracite or lignite coal-fired industrial boilers.

An average SO_3 emission factor for bituminous coal-fired boilers has been calculated using the KVB and Monsanto data and is presented in Table 30. Also presented in Table 30 are severity factors for SO_3 emissions from various combustion systems estimated using this emission factor. As shown in this table, emissions of SO_3 are environmentally significant--with mean severity factors well in excess of 1.0--for all of the industrial combustion systems studied. Because of the high variability of SO_3 emissions data for industrial combustion systems and the environmental significance of these emissions, the SO_3 emissions data base must be considered inadequate.

TABLE 29. SUMMARY OF SO_3 EMISSIONS DATA FOR BITUMINOUS COAL-FIRED BOILERS

Combustion system	Percent of fuel sulfur emitted as SO_3	Reference
Pulverized, dry	0.11	25
Pulverized, dry	0.76	17
Spreader stoker	2.1	17
Spreader stoker	0.3	23
Average	0.81	
Variability (percent)	174	

TABLE 30. EMISSION FACTORS AND AMBIENT SOURCE SEVERITY FACTORS FOR SO_3 FROM BITUMINOUS COAL-FIRED INDUSTRIAL BOILERS

Combustion System	SO_3 emission factor (ng/J)	Mean severity factor[a]	Upper limit severity factor[a]
Pulverized, dry	7.95 S[b]	2.23	6.11
Cyclone	7.95 S	2.23	6.11
Spreader stoker	7.95 S	1.67	4.58
Other stoker	7.95 S	2.59	7.09

[a] Based on heat capacities of 200 GJ/hr for pulverized coal-fired boilers and cyclones, 150 GJ/hr for spreader stokers, and 50 GJ/hr for other stokers; and stack heights of 50 meters for pulverized coal-fired boilers, cyclones, and spreader stokers, and 23.2 meters for other stokers.

[b] S indicates the percentage of sulfur present in the fuel. The emission factor presented is based on an average fuel sulfur content of 1.92 percent.

Sulfate emissions data are available only for the pulverized coal-fired boiler tested by Monsanto.[25] The fraction of fuel sulfur emitted as sulfates (including H_2SO_4) during these tests was about 0.13 percent. This corresponds to an emission factor for sulfate in nanograms per joule of about 1.27 S, where S represents fuel sulfur content in percent. Because no data are available to determine the variability of these emissions, the data base for sulfate emissions from industrial coal-fired systems is also considered inadequate.

Emissions of SO_3 and sulfates from industrial boilers are expected to be similar to emissions from utility boilers. Data for bituminous coal-fired utility boilers show an average conversion of fuel sulfur to primary sulfate of 1.5 percent, where primary sulfate is defined to include SO_3, sulfuric acid and sulfate salts (such as metallic sulfates and ammonium sulfate).[28] The data also indicate that approximately equal amounts of fuel sulfur are converted to SO_3 and sulfate (sulfuric acid and sulfate salts). Thus SO_3 emissions data for industrial boilers[25] and utility boilers[28] are in approximate agreement. However, sulfate emissions from utility boilers are much higher than that measured in the Monsanto industrial boiler test.

4.1.4.4 Trace Element Emissions--

Trace element emissions from coal-fired combustion systems are determined by the concentrations of trace elements in the coal burned, and the partitioning patterns of the elements between the bottom ash, the fly ash and the gas phase. Trace elements present in coal have been classified in three main groups based on their partitioning behavior.[29] Class I include elements that are approximately equally concentrated in the fly ash and the bottom ash, Class II includes elements that are enriched in the fly ash relative to their concentrations in the bottom ash, and Class III includes elements that are emitted in the gas phase. The partitioning behavior of a particular element is determined by the volatility and adsorptive properties of its compounds. Most of the trace elements present in coal fall into Class I. Class II elements include antimony, arsenic, cadminum, copper, gallium, lead, molybdenum, sulfur and zinc; and Class III elements include bromine, chlorine, and mercury.[29]

The data base for trace element emissions from coal-fired industrial boilers is limited. Emission rates of a wide variety of elements from a pulverized bituminous coal-fired boiler were measured by Monsanto Research Corporation.[25] Also, trace element mass balance and emissions data have been developed by KVB for a chain grate stoker and a pulverized coal-fired system.[30] However, these data pertain only to the coal types that were burned during testing.

Trace element emissions from industrial boilers are expected to be similar to trace element emissions from utility boilers, for which an extensive data base has been developed. Estimated emission factors and source severities are presented in Table 31 for uncontrolled and controlled trace element emissions from bituminous coal-fired pulverized and spreader stoker industrial combustion systems. These data were estimated using data developed in Reference 28 for utility boilers. The utility boiler data are based on average trace element concentrations for various types of coal, and trace element partition factors calculated from test data.

The emission factors presented in Table 31 should be considered estimates, because the assumption was made that emissions from industrial boilers can be compared to emissions from much larger utility boilers. Also, the utility boiler data in Reference 28 were based mainly on test data for pulverized systems controlled by electrostatic precipitators. Thus, additional assumptions were made in calculating controlled emission factors and emission factors for spreader stokers. These assumptions were that the behavior of trace elements in cyclone control devices is similar to that in electrostatic precipitators and that the trace element partitioning in a spreader stoker system is similar to that in a pulverized system. Although these assumptions are not strictly correct, the estimated emission factors in Table 31 should provide a good indication of the relative environmental significance of trace elements from industrial boilers.

As shown in Table 31, emissions of a number of elements from industrial boilers are environmentally significant. Controlled emissions of several elements, are associated with severities exceeding 0.05, and uncontrolled emissions of a number of elements and controlled emissions of chlorine are associated with severity factors in excess of 1.0. Because of the lack of

TABLE 31. ESTIMATED TRACE ELEMENT EMISSION FACTORS AND AMBIENT SEVERITY FACTORS FOR BITUMINOUS COAL-FIRED BOILERS

	Pulverized[a]				Spreader stoker[b]			
	Uncontrolled		Controlled[c]		Uncontrolled		Controlled[c]	
	Emission factor (ng/J)	Mean ambient severity[d]	Emission factor (ng/J)	Mean ambient severity[d]	Emission factor (ng/J)	Mean ambient severity[e]	Emission factor (ng/J)	Mean ambient severity[e]
Aluminum	397	4.8	119	1.4	304	2.7	91	0.81
Antimony	0.2	0.049	0.048	0.05	0.15	0.027	0.037	0.081
Arsenic	1.2	2.9	0.35	0.87	0.92	1.7	0.27	0.51
Barium	4.2	1.0	1.25	0.30	3.2	0.57	0.96	0.17
Beryllium	0.1	6.1	0.031	1.8	0.077	8.5	0.024	1.1
Boron	4.1	0.050	1.24	0.015	3.1	0.29	0.95	0.087
Bromine	0.34	0.059	0.34	0.018	0.34	0.34	0.34	0.10
Cadmium	0.08	0.20	0.024	0.060	0.061	0.11	0.018	0.033
Calcium	263	6.4	78.8	1.9	201	3.7	60.3	1.1
Chlorine	33.9	1.4	33.9	0.42	33.9	0.80	33.9	0.24
Chromium	2.6	6.3	0.77	1.9	2.0	3.6	0.59	1.1
Cobalt	0.4	0.98	0.11	0.30	0.31	0.56	0.084	0.17
Copper	1.1	0.13	0.32	0.039	0.84	0.074	0.24	0.022
Fluorine	13.5	0.83	4.06	0.25	10.3	0.47	3.1	0.14
Iron	393	9.6	118	2.9	301	5.4	90.3	1.6
Lead	0.9	0.73	0.28	0.22	0.69	0.42	0.21	0.13
Lithium	1.13	6.3	0.34	1.9	0.86	3.6	0.26	1.1
Magnesium	57	0.70	17.2	0.21	43.6	0.40	13.2	0.12
Manganese	1.8	0.044	0.54	0.013	1.38	0.025	0.41	0.008
Mercury	0.007	0.017	0.007	0.005	0.007	0.010	0.007	0.003
Molybdenum	0.5	0.012	0.15	0.004	0.38	0.007	0.11	0.002
Nickel	2.9	3.5	0.87	1.1	2.2	2.0	0.67	0.60
Phosphorus	4.9	5.9	1.48	1.8	3.7	3.4	1.1	1.0
Potassium	53	3.2	15.8	0.96	40.5	1.8	12.1	0.54
Selenium	0.3	0.18	0.10	0.054	0.23	0.10	0.077	0.03
Silicon	711	8.6	213	2.6	544	4.8	163	1.5
Sodium	24	1.2	7.16	0.36	18.4	0.68	5.48	0.20
Strontium	7.0	0.28	2.1	0.084	5.4	0.16	1.6	0.048
Thorium	0.06	0.17	0.02	0.051	0.05	0.10	0.01	0.030
Tin	0.5	0.012	0.15	0.004	0.38	0.007	0.11	0.002
Uranium	0.04	0.024	0.012	0.007	0.03	0.014	0.009	0.004
Vanadium	1.3	0.32	0.38	0.096	0.99	0.18	0.29	0.054
Zinc	2.0	0.048	0.61	0.014	1.5	0.027	0.47	0.008

[a] Calculated from data in Reference 28, Table 59.

[b] Calculated from emission factors of bituminous, pulverized, dry-bottom boilers and the ratio of published EPA emission factors for pulverized, dry-bottom boilers and spreader stokers.

[c] Cyclone

[d] Based on a heat capacity of 100 GJ/hr.

[e] Based on a heat capacity of 50 GJ/hr.

trace element emissions data for coal-fired industrial boilers, and because of the potential environmental significance of these emissions, additional data for trace element emissions are needed.

4.1.4.5 Specific Organic and POM Emissions--

Emissions of specific POM from bituminous coal-fired industrial boilers have been measured by the Public Health Service and by Monsanto Research Corporation.[18,25] No data were found in the literature for POM emissions from anthracite- or lignite-fired industrial boilers. In the Public Health Service tests, samples were collected by chilling the flue gas and passing it through a high efficiency filter. Organic matter was extracted from the filter catch with benzene and separated into fractions using chromatography, Concentrations of specific organics were measured using ultraviolet-visible spectroscopy.[18] In the Monsanto tests, samples were collected using a Source Assessment Sampling System (SASS) train, which uses cyclones to capture particulate matter and XAD-2 resin to capture gaseous organic species. Polycyclic species were extracted using methylene chloride, and concentrations of specific organics were determined using combined gas chromatography/mass spectroscopy.[25]

The results of these tests are shown in Table 32. Variabilities and severity factors for the data were not calculated because of the limited number of tests and the variations in fuel used, boiler load, and combustion method. The data base for POM emissions from coal-fired industrial boilers is considered inadequate.

4.1.5 Existing Emissions Data; Wood-Fired Sources

The pollutant emissions data base for wood-fired combustion is growing as a result of an increased interest in wood as a fuel and increased efforts by EPA to fill existing data gaps. The inadequacy of the data base is, in some measure, due to the variability of wood fuel as fired in a number of combustion system designs. Information concerning wood-fired combustion systems and pertinent properties of wood, e.g., chemical composition, average moisture content and thermal properties, can be found in references 31-33. This information, while useful in assessing the potential impact of emissions from wood combustion, cannot be directly related to emissions from specific sources.

TABLE 32. POM EMISSIONS FROM BITUMINOUS COAL-FIRED INDUSTRIAL BOILERS, (pg/J)

Pollutant	Combustion system				
	Pulverized with ESP, 132 GJ/hr[a]	Pulverized with multiclone, 137 GJ/hr[b]	Uncontrolled chain grate stoker 155 GJ/hr[c]	Spreader stoker with multiclone, 62.5 GJ/hr[d]	Uncontrolled underfeed stoker, 4.6 GJ/hr[e]
Total benzene soluble organics	NM	2749	1800	5118	2844
Pyrene	ND	0.23	0.37	0.56	15
Benzo(a)pyrene	ND	0.030	0.035	0.025	9.5
Benzo(e)pyrene	ND	0.087	0.12	0.33	7.4
Perylene	ND	ND	ND	ND	1.5
Benzo(g,h,i)pyrene	ND	ND	ND	ND	4.2
Anthanthrene	ND	ND	ND	ND	0.27
Coroncene	NM	ND	ND	0.025	0.31
Anthracene	[5.3]	0.35	ND	ND	0.81
Phenanthrene		ND	ND	ND	9.5
Fluoranthrene	5.4	0.52	0.65	0.34	36.
Dibenzothiophene	0.13	NM	NM	NM	NM
Methylanthracenes/phenanthrenes	0.33	NM	NM	NM	NM
Dimethylanthracenes/phenanthrenes	0.10	NM	NM	NM	NM
Methylfluoranthrenes/pyrenes	0.63	NM	NM	NM	NM
Benzo(c)phenanthrene	0.16	NM	NM	NM	NM
Dimethylbenz(a)anthracenes	0.97	NM	NM	NM	NM
Methylcholanthrenes	2.8	NM	NM	NM	NM
Indeno(1,2,3-c,d)pyrene	0.10	NM	NM	NM	NM
Benzofluoranthrenes	11.	NM	NM	NM	NM
Dibenz(a,h)anthracene (or isomers)	0.43	NM	NM	NM	NM
Dibenzo(c,g)carbazole	ND	NM	NM	NM	NM
Dibenzopyrenes	0.73	NM	NM	NM	NM
Methylchrysenes (or isomers)	1.2	NM	NM	NM	NM

ND -- not determined.
NM -- not measured.

[a] Reference 25. Watertube boiler with 132 GJ/hr fuel capacity; operating load is not known.

[b] Reference 18. Watertube boiler at 53 percent load.

[c] Reference 18. Watertube boiler at 89 percent load.

[d] Reference 18. Watertube boiler at 70 percent load.

[e] Reference 18. Firetube boiler at 61 percent load.

4.1.5.1 Criteria Pollutant Emissions--

Particulate emissions data for boilers fired by combinations of wood fuels have been compiled by the Oregon Department of Environmental Quality.[34,35] Also, emissions from wood and wood waste boilers have been measured by the Vermont Agency of Environmental Conservation.[36] Appendix C presents the data which were obtained at baseline conditions (approximately 80 percent load) for boilers fired by combinations of wood and bark. Available information on boiler operating conditions and fuel composition is also presented. The wood/bark combustion systems for which particulate emissions data are available can be divided into dutch oven systems, which generally use firetube boilers, and stoker systems, which generally use watertube boilers. Emissions data for these two categories are summarized in Table 33. The dutch oven systems tested ranged in size from 2.4 GJ/hr to 88 GJ/hr input capacity, while the stokers tested ranged from 30 GJ/hr to 150 GJ/hr input capacity. As noted in Chapter 3, wood-fired boilers are often installed with attached multiclones for particulate control or fly ash reinjection. Therefore, emissions data are summarized in Table 33 for uncontrolled units, multiclone controlled units with fly ash reinjection, and multiclone controlled units without fly ash reinjection. For each boiler type and emission control method, the table presents the number of units tested, the average emission factor for the tested units, the variability and the severity factor associated with the emission factor, and an assessment of the data base adequacy. Also, for comparison, the published EPA emission factor range for uncontrolled wood/bark boilers is presented.[9]

The data indicate that particulate emissions are environmentally significant for uncontrolled dutch ovens, and for both multiclone controlled and uncontrolled stokers. The variabilities of the mean emission factors for multiclone controlled stokers and for controlled and uncontrolled dutch ovens are below 70 percent. Therefore, the data base for these wood-fired combustion systems is considered adequate. The variability of the mean emission factor for uncontrolled stokers, however, is well above 70 percent, and thus the data base for uncontrolled stokers must be considered inadequate.

TABLE 33. SUMMARY OF PARTICULATE EMISSIONS DATA FOR WOOD-FIRED BOILERS

Combustion system/ particulate collection	Number of data points	Mean emission factor (ng/J)	Variability (percent)	Ambient severity factor[a]	Data base adequacy[b]	EPA emission factor[c]
Dutch oven						
No control	30	370	46	0.068	A	490-2450
Multiclone	11	215	30	0.039	A	--
Multiclone, flyash reinjection	12	239	41	0.044	A	--
Stoker						
No control	3	600	211	0.34[d]	I	490-2450
Multiclone	8	337	61	0.062	A	--
Multiclone, flyash reinjection	10	527	23	0.097	A	--

[a] Based on a heat input capacity of 8.5 GJ/hr and a stack height of 30 meters.

[b] Adequate data base is indicated by A and inadequate data base is indicated by I.

[c] Based on a wood heating value of 10,227 kJ/kg.

[d] Upper limit severity factor.

SO_2 emission rates were measured for four large bark-fired boilers by the National Council of the Paper Industry for Air and Stream Improvement (NCASI).[37] These boilers were stokers ranging in size from 160 GJ/hr to 270 GJ/hr input capacity. The results of these tests are presented in Appendix C and summarized in Table 34. The tests indicated that about 5 percent of the sulfur present in the bark was emitted in the flue gas as SO_2, while the remaining 95 percent exited the boiler in the form of sulfate in either the fly ash or the bottom ash. The high conversion of sulfur to sulfate was attributed by NCASI to the alkaline nature of wood ash and high excess air levels generally used for wood/bark boilers. The high excess air levels result in relatively low combustion temperatures which cause the SO_3 formation to be more thermodynamically favored than in oil or coal-fired boilers. The published EPA emission factor, shown in Table 34 for comparison, is based on the assumption that about 50 percent of the sulfur present in wood is emitted in the flue gas.

As shown in Table 34, the data base for SO_2 emissions from wood/bark boilers meets the criteria for data base adequacy. The variability of the mean emission factor is well below 70 percent, and the ambient severity associated with the mean emission factor is less than 0.001.

NO_x emission rates for wood/bark boilers have been measured by the State of Vermont,[36] TRW Environmental Engineering Division,[38] Monsanto Research Corp.,[39] and NCASI.[40] The boilers tested were dutch oven units and stokers, and, ranged in size from 5.8 GJ/hr to 400 GJ/hr input capacity. The results of the tests are presented in Appendix C and summarized in Table 34. These results indicate that the NO_x emission factor, in terms of mass of NO_x per unit boiler heat input, increases dramatically with the boiler heat input capacity. Emission factors were in the range of 5-10 ng/J for small boilers (about 10 GJ/hr input capacity) and in the range of 50-100 ng/J for large boilers (greater than 30 GJ/hr input capacity). As indicated in Table 34, the mean NO_x emission factor from the literature data is much lower than the published EPA NO_x emission factor.[9] This may be the result of differences in operating conditions, as the units tested by Vermont and TRW were operated at very high excess air levels (up to 500 percent).

TABLE 34. SUMMARY OF SO_2, NO_x, AND HYDROCARBON EMISSIONS DATA FOR WOOD-FIRED BOILERS

Pollutant	Number of units tested	Mean emission factor (ng/J)	Variability (percent)	Ambient severity factor[a]	Data base adequacy[b]	EPA emission factor[c] (ng/J)
SO_2	4	71.0S[d]	28	<0.001	A	735S[d]
NO_x (as NO_2)	23	43.3	33	0.025	I	489
Hydrocarbons	6	63.2	71	0.046[e]	A	100-3400

[a] Based on a heat input capacity of 8.5 GJ/hr and a stack height of 30 m.

[b] Adequate data base is indicated by A and inadequate data base by I.

[c] Assuming a wood heating value of 10,227 kJ/kg.

[d] S refers to the fuel sulfur content in percent.

[e] Upper limit severity factor.

As shown in Table 34, the data base for NO_x emissions from wood/bark-fired boilers satisfies the criteria for data base adequacy. The variability of the mean NO_x emission factor is below 70 percent, and the ambient severity factor associated with the mean emission factor is 0.025, which is less than the 0.05 level considered to represent environmental significance. However, because the severity factor is close to 0.05, and because the emission factor derived from the literature is lower than the published EPA emission factor by an order of magnitude, the data base is considered inadequate.

Hydrocarbon emissions from a number of dutch oven and stoker wood/bark boilers have been measured by the Oregon Department of Environmental Quality.[41] The units tested ranged in size from 11 to 72 GJ/hr output steam capacity. The test results are presented in Appendix C and summarized in Table 34. Table 34 shows the number of sources tested, the mean emission factor, variability, the ambient severity factor associated with the mean emission factor, an assessment of the data base adequacy, and, for comparison, the published EPA emission factor for hydrocarbons.[9]

As shown in Table 34, the data base for hydrocarbon emissions from wood/bark-fired boilers is considered adequate. Although the variability of the mean emission factor derived from the literature exceeds 70 percent, the upper limit severity factor is below 0.05. Also, when the variability of the emission factor derived from literature is taken into account, this emission factor is an agreement with the lower range of the EPA published emission factor.

No data on CO emissions from wood or wood waste combustion were found in the literature. Therefore, the data base for CO emissions from wood/bark boilers must be considered inadequate.

4.1.5.2 Fine Particulate Emissions--

Particle size distribution data by mass were obtained by the State of Vermont for five uncontrolled dutch ovens and 2 uncontrolled stokers,[36] and by Monsanto Research Corp. for a cyclone controlled stoker with fly ash reinjection.[39] These data are summarized in Table 35.

TABLE 35. PARTICLE SIZE DISTRIBUTION DATA FOR WOOD-FIRED BOILERS

	Fraction of particulates in aerodynamic size range		
	<1 μm	<3 μm	<10 μm
Dutch oven-uncontrolled			
Average (16 tests)[a]	0.42	0.53	0.71
Variability	27%	25%	13%
Range	0.0-0.63	0.6-0.88	0.42-0.88
Stoker-uncontrolled			
Average (6 tests)[b]	0.18	0.25	0.42
Variability	120%	99%	58%
Range	0.019-0.49	0.065-0.58	0.21-0.72
Stoker-multiclone control			
Average (6 tests)[c]	0.19	0.45	0.76
Variability	79%	31%	12%
Range	0.02-0.43	0.33-0.68	0.65-0.92

[a] Four boilers were tested three times each and one boiler was tested four times for a total of 16 tests.

[b] Two boilers were tested three times each for a total of six tests.

[c] One boiler was tested six times.

Percentages of respirable particles (particles smaller than about 3 μm) average about 53 percent for the uncontrolled dutch ovens, 25 percent for the uncontrolled stokers, and 45 percent for the controlled stoker. As Table 35 shows, the mean fractions of particles smaller than 1 μm, 3 μm, and 10 μm for uncontrolled dutch ovens have variabilities well below 70 percent for the small size ranges. Therefore, the particle size distribution data for dutch ovens are considered adequate. The particle size data for uncontrolled and controlled stokers have variabilities higher than 70 percent for the small size ranges. For this reason, and because only a few stokers have been tested, the particle size data base for stokers must be considered inadequate.

4.1.5.3 SO_3 and Sulfate Emissions--

In addition to measuring SO_2 emissions from bark-fired boilers, NCASI also measured particulate sulfate concentrations in the bottom ash, the primary cyclone collector catch, and the flyash emitted from the boilers.[37] Particulate sulfate emissions were successfully measured for three of the four boilers tested by NCASI. These units were cyclone controlled stokers ranging in size from 150 GJ/hr to 270 GJ/hr heat input. The particulate sulfate emissions data obtained by NCASI are presented in Table 36. This table also gives the mean particulate sulfate emission rate and the variability associated with this emission factor. The mean emission factor corresponds to the emission as particulate sulfates of about 67 percent of the fuel sulfur. The variability of the mean emission factor is well above 70 percent and the upper limit ambient severity derived from the emissions data is 0.57. Thus, the data base for particulate sulfate emissions from wood/bark boilers must be considered inadequate. No data were found in the literature for gaseous SO_3 emissions from wood/bark boilers.

TABLE 36. PARTICULATE SULFATE EMISSIONS DATA FOR BARK-FIRED BOILERS.

Boiler	Particulate sulfate emissions	Fuel sulfur content	Fuel ash content
Unit 1	1050S ng/J	0.068%	1.3%
Unit 2	388S ng/J	0.010%	1.3%
Unit 3	1090S ng/J	0.060%	2.5%
Mean	842S ng/J		
Variability	116%		

S refers to the fuel sulfur content in percent.

4.1.5.4 Trace Element Emissions--

No data were found in the literature on trace element emissions from wood- or wood-waste - fired boilers. However, fly ash from a wood-fired stoker caught in a primary cyclone collector was analyzed for trace elements by the State of Vermont.[36] The results of these tests are presented in Table 37. Also presented in this table are estimates of trace element emission factors and mean ambient severity factors for uncontrolled stokers and multiclone controlled stokers without flyash reinjection. These emission factors and mean severities were obtained using the particulate emission factors presented in Table 33, with the assumption that the trace element content of emissions will be similar to that of the primary collector catch. However, because the more volatile trace elements would become concentrated in smaller particles which would penetrate the primary collection system, emissions of some trace elements may be higher than Table 37 indicates. As shown in Table 37, the only trace element associated with an ambient severity greater than 0.05 is magnesium, with a severity factor of 0.093. However, since the severity factors presented in the table are based on an analysis of captured flyash rather than flyash emissions, the data base for all trace element emissions from wood/bark boilers must be considered inadequate.

4.1.5.5 Specific Organic and POM Emissions--

The specific organic and POM emissions data base for wood and wood-waste boilers is limited to data for benzo(a)pyrene (BaP) emissions collected by Monsanto Research Corp.[39] Monsanto measured BaP emissions for a bark-fired

TABLE 37. ESTIMATED EMISSION FACTORS AND AMBIENT SEVERITY FACTORS OF TRACE ELEMENTS FROM WOOD-FIRED STOKERS

Element	Cyclone catch concentration[a] (mg/g)	Estimated emission factors for wood-fired stokers (ng/J)[b]		Ambient severity factors[c]	
		No control	Controlled (w/o reinjection)	No control	Controlled (w/o reinjection)
Aluminum	16.	9.6	5.4	0.004	0.002
Cadmium	0.0075	0.0045	0.0025	<0.001	<0.001
Calcium	420	250	140	0.006	0.003
Chromium	0.11	0.066	0.037	<0.001	<0.001
Cobalt	0.040	0.024	0.013	0.005	0.003
Copper	0.11	0.066	0.037	<0.001	<0.001
Iron	22.	13.	7.4	0.004	0.002
Lead	0.082	0.049	0.028	0.002	0.001
Magnesium	390	230	130	0.093	0.052
Manganese	21.	12.6	7.1	0.007	0.004
Nickel	0.094	0.056	0.032	0.001	<0.001
Potassium	16.	9.6	5.4	<0.001	<0.001
Sodium	4.3	2.6	1.4	<0.001	<0.001
Strontium	0.54[d]	0.31	0.18	<0.001	<0.001
Vanadium	0.13[d]	0.078	0.044	<0.001	<0.001
Zinc	0.42	0.25	0.14	0.001	<0.001

[a] Unless otherwise noted, concentrations were measured using atomic absorbtion.

[b] Calculated using average particulate emission factors from Table 33.

[c] Based on a heat input capacity of 8.5 GJ/hr and a stack height of 30 meters.

[d] Concentrations measured using X-ray fluorescence.

spreader stoker controlled by a cyclone and a venturi scrubber in series. BaP concentrations were measured concurrently in the stack gas entering and leaving the venturi scrubber. BaP was collected by passing the stack gas through a heated filter and a tube filled with XAD-2 resin. The BaP was then extracted from the filter and the resin using cyclohexane and methylene chloride, respectively; BaP concentrations in the solvents were measured using fluorescence spectrophotometry.

The results of the Monsanto BaP tests are summarized in Table 38. This table presents, for the cyclone controlled stack gas and the cyclone and scrubber controlled stack gas, the ranges of emission factors, the mean emission factors, and the variabilities associated with the mean emission factors. The Monsanto results indicate that the secondary scrubber did not reduce BaP emissions. In fact, on the average, the measured concentration of BaP entering the scrubber was lower than the measured concentration leaving it. The difference is, however, within the range of the variability of the data. The variability was 133 percent for measurements conducted upstream of the scrubber and 126 percent for measurements conducted downstream of the scrubber.

Because of this high variability, and because the Monsanto tests were for a single boiler, the data base for BaP emissions from wood- and wood-waste boilers must be considered inadequate. As noted above, no data were found in the literature on emissions of other specific organics or POM.

TABLE 38. BaP EMISSIONS DATA FOR A BARK-FIRED STOKER.

	Cyclone controlled emissions	Scrubber controlled emissions
Number of tests	6	6
Emission factor range (pg/J)	0.00-0.047	0.00-0.067
Mean emission factor (pg/J)	0.014	0.022
Variability (percent)	133	126

4.2 EMISSION DATA ACQUISITION

4.2.1 Selection of Test Facilities

The evaluation of existing emissions data for industrial combustion sources has shown that the existing data base is generally inadequate. To correct these deficiencies, a total of 32 sites were selected for sampling and analysis of flue gas emissions.

In general, the assignment of the number of test sites to each source category was based on consideration of three factors: fuel consumption within the industrial sector, potential significance of the impact caused by flue gas emissions, and inadequate characterization of flue gas emissions. Thus, more bituminous coal-fired sites were selected for testing than were warranted by fuel consumption because of the known high NO_x, SO_2 and particulate emissions from these sources, and the inadequate characterization of fine particulate, trace element and organic emissions from these same sources. Similarly, five wood-fired sources, a number far greater than that warranted by fuel consumption alone, were selected for testing because of the inadequate characterization of most pollutants from wood-fired sources and the high POM emissions found in an earlier test of a wood-fired commercial/institutional combustion source.[42]

The choice of specific sites was based on the representativeness of the sites as measured against the important characteristics of systems within each source category. Firing method, unit capacity and age were the principal characteristics considered. When several sites within a source category were selected for testing, a range of these characteristics was generally chosen. For example, the gas-fired sites tested include three firetube and seven watertube units. The capacity and age of the firetube units tested were 8, 15, and 25 GJ/hr and 23, 22, and 6 years old in age, respectively. The watertube units ranged in capacity from 36 to 178 GJ/hr and in age from 7 to 50 years. Consistent with industrial practice, no control devices were used with these units.

The rated thermal output capacity, manufacturer, burner and boiler type and pollution control method, as appropriate for the 32 sources tested, are presented in Tables 39, 40, and 41. As shown in the tables, the gas-

TABLE 39. CHARACTERISTICS OF INDUSTRIAL GAS-FIRED EXTERNAL COMBUSTION SOURCES SELECTED FOR TESTING

Site No.	Manufacturer	Boiler type	Rated capacity[a] (GJ/hr)	Rated capacity[a] (MW)	Age as of 1979 (years)	Pollution control device
150	Cleaver Brooks	Packaged firetube	25	7.3	6	None
151	Kewanee	Packaged scotch	8	2.4	23	None
157	Combustion Engineering	Field watertube	178	52	50	None
158	Wicks	Packaged firetube	5	4.4	22	None
159	Babcock & Wilcox	Field watertube	72	21	28	None
161	Babcock & Wilcox	Field watertube	72	21	28	None
162	Babcock & Wilcox	Field watertube	72	21	28	None
328	Bigelow Co.	Field watertube	36	10.5	12	None
334	Babcock & Wilcox	Field watertube	61	18	13	None
335	Combustion Engineering	Field watertube	61	18	7	None

[a] Output capacity.

TABLE 40. CHARACTERISTICS OF INDUSTRIAL OIL-FIRED EXTERNAL COMBUSTION SOURCES SELECTED FOR TESTING

Site No.	Manufacturer	Fuel No.	Burner type	Boiler type	Rated capacity[a] (GJ/hr)	(MW)	Age as of 1979 (years)	Pollution control device
152	C.E. Natco	b	Steam	Drumless serpentine	43	12.6	6	None
153	C.E. Natco	b	Steam	Same	43	12.6	6	None
160	Babcock & Wilcox	5	Steam	Field watertube	78	23	28	None
163	Babcock & Wilcox	5	Steam	Field watertube	78	23	28	None
170	-	2	-	Field watertube	116	32.1	-	None
172	-	2	-	Field watertube	155	43.1	-	None
173	-	2	-	Field watertube	42	11.5	-	None
174	Babcock & Wilcox	2	-	Field watertube	107	29.7	-	None
202/203	Babcock & Wilcox	6	-	Field watertube	117	34	12	Multiclone followed by double alkali FGD unit 99.4% Eff. for part.; 96.7% Eff. for SO_2

[a] Output capacity.

[b] Kern River Crude.

TABLE 41. CHARACTERISTICS OF INDUSTRIAL SOLID FUEL-FIRED EXTERNAL COMBUSTION SOURCES SELECTED FOR TESTING

Combustion source type	Site No.	Manufacturer	Rated capacity[a] (GJ/hr)	(MW)	Age as of 1979 (years)	Pollution control device
Bituminous, pulverized wet bottom	223	Babcock & Wilcox	247	72	25	Multiclone followed by ESP. 99.7% est. o/a eff.
Bituminous, pulverized wet bottom	224	Babcock & Wilcox	185	54	32	Multiclone at 90% est. eff.
Bituminous, pulverized wet bottom	225	Babcock & Wilcox	185	54	32	Multiclone at 90% est. eff.
Bituminous, pulverized dry bottom	200/201	Babcock & Wilcox	117	34	12	Multiclone followed by double alkali FGD unit 99.4% eff. for part.; 96.7% eff. for SO_2.
Bituminous, pulverized dry bottom	341	Combustion Engineering	256	75	13	ESP at 99% est. eff.
Bituminous, spreader stokers	221	Wickes	158	46	23	Multicyclone followed by ESP. 99.5% est. o/a eff.
Bituminous, spreader stokers	226	Babcock & Wilcox	131	38.4	27	Multiclone at 90% est. eff.
Bituminous, spreader stokers	340	Babcock & Wilcox	153	45	27	2-multicyclones at 95% est. o/a eff.
Wood stokers[b]	145	Wellons-Birchfield	13	3.7	12	None
Wood stokers	146[c]	Puget Sound Machinery	57	16.8	31	Scrubber 90% est. eff.
Wood stokers	147[c]	Erie City Iron Works	97	28.4	19	Scrubber 90% est. eff.
Wood stokers	148	Babcock & Wilcox	43	12.6	29	None
Wood stokers	149[d]	Wellons, Inc.	18.5	5.4	11	None

[a] Output capacity.

[b] Underfeed stokers unless otherwise noted.

[c] Dutch oven design.

[d] Fluid bed design.

and distillate oil-fired sites were not equipped with control devices; only one residual oil site (Site 200/201) was equipped with a control device, a pilot double alkali FGD unit; two of the wood-fired sites were equipped with scrubbers and all coal-fired sites were equipped with either multiclones, ESPs, or the pilot FGD unit evaluated during coal combustion at Site 202/203.

4.2.2 Field Testing

Field testing procedures were based on Level I environmental assessment methods. The Source Assessment Sampling System (SASS) was used to collect particulate, organic and trace metal samples. The SASS train (Figure 4) is a high volume (5 scfm) system designed to extract particulates and gases from the flue gas stream, separate particulates into four size fractions, trap organics in an adsorbent, and collect volatile trace metals in liquid solutions. The high sampling volume is required to collect adequate quantities of trace materials for subsequent laboratory analysis. The train is constructed so that all sample contacting surfaces are type 316 stainless steel, Teflon, or glass.

In accordance with the program Procedures Manual, the cyclones were not used at the gas- and oil-fired sources because of low concentrations of particulates and their characteristic small particle diameters for these fuels. In all tests, however, particulates were collected on Spectrograde glass fiber filters in the heated oven. The sample stream was then cooled and the organic material collected by adsorption on XAD-2 resin (a styrene, divinylbenzene copolymer). The gas then passed through an impinger containing hydrogen peroxide to collect oxidizable constituents. The second and third impingers, containing ammonium peroxydisulfate and silver nitrate, were used to collect volatile trace elements. A fourth impinger containing silica gel was used to remove the remaining moisture from the gas stream.

Samples of the flue gas were obtained at a single traverse point approximating the average flow rate of the flue gas, as determined by a multipoint traverse. Sampling time for the SASS train was from 4 to 6 hours as required to obtain a total sample volume of 30 cubic meters or greater. Sample recovery was carried out in a clean environment according to Level 1 specifications.

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*This procedures manual was developed specifically for this program and is not an approved IERL-RTP procedures manual.

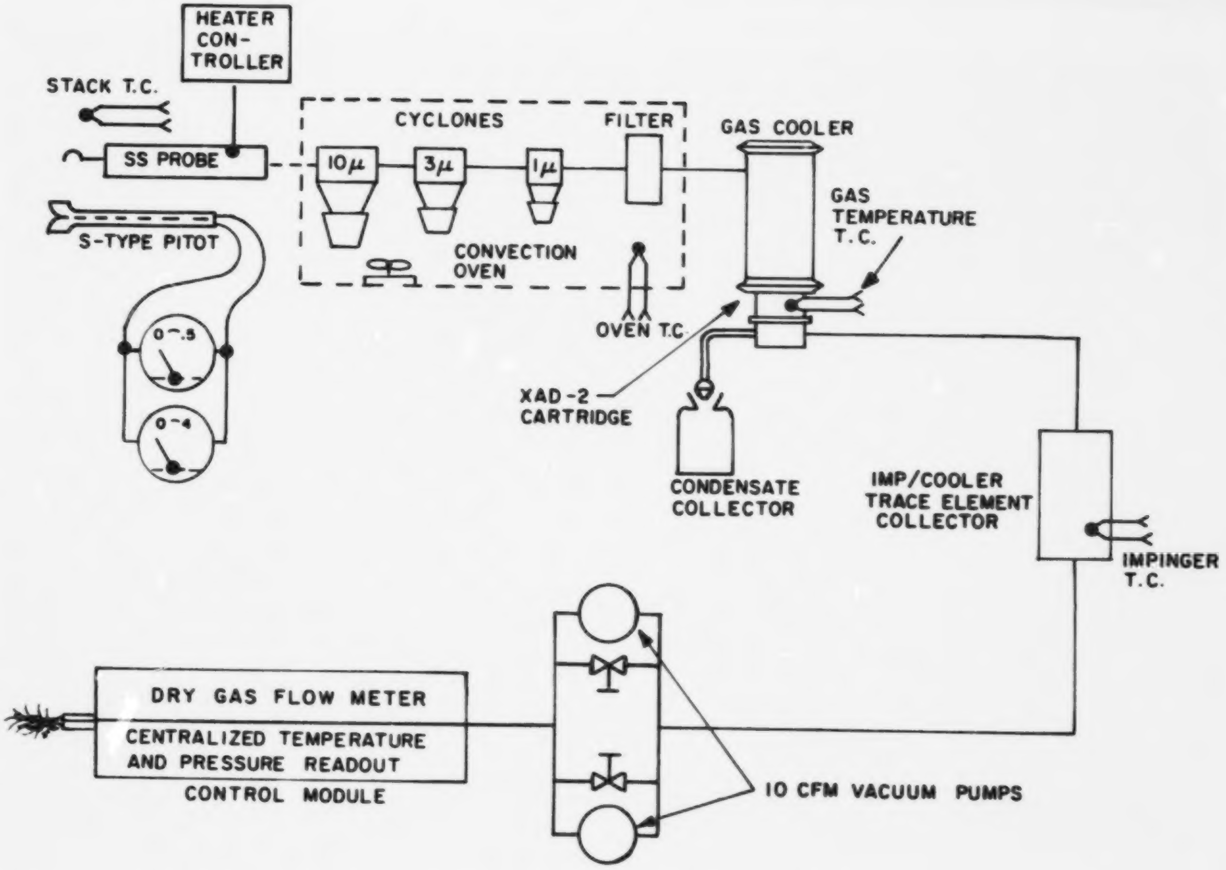

HEATER CON-TROLLER
STACK T.C.
SS PROBE
S-TYPE PITOT
0-.5
0-4
CYCLONES
10μ
3μ
1μ
FILTER
CONVECTION OVEN
OVEN T.C.
GAS COOLER
GAS TEMPERATURE T.C.
XAD-2 CARTRIDGE
CONDENSATE COLLECTOR
IMP/COOLER TRACE ELEMENT COLLECTOR
IMPINGER T.C.
DRY GAS FLOW METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
10 CFM VACUUM PUMPS

Figure 4. SASS Train.

Modified Level I field tests were conducted at the stack for 32 industrial combustion sources. The operating load and fuel feed rates for the sites tested are presented in Table 42. Twenty-seven of the sites were tested at energy input levels ranging from 60 to 106 percent of design capacity. The other tests were conducted under significantly derated conditions: as low as 20 percent of design capacity for a stoker unit burning wood (site 149).

Samples of the flue gas were also collected in Tedlar gas sampling bags, using a stainless steel probe, condenser, and diaphragm pump, for onsite analyses of flue gas constituents. The gas in the bag was injected into a gas chromatograph through a heated gas sampling valve. Low molecular weight hydrocarbons were analyzed using a flame ionization detector, measuring the resulting peaks for retention times and areas, and comparing these against a known series of C_1-C_6 n-alkane standards for qualitative and quantitative analysis. Carbon monoxide, CO_2, O_2, and N_2 were measured using a thermal conductivity detector and standard mixes of these gases for calibration.

Sampling of the flue gas for NO_x was conducted either by EPA Method 7 (40-CFR-60, Appendix A, Method 7) or by chemiluminescence at several solid fuel-fired units.

4.2.3 Laboratory Analysis Procedures

The procedures described in this section are designed to be an integral part of the phased environmental assessment approach and apply primarily to Level I. The purpose of the initial phase is to obtain preliminary environmental assessment information, identify problem areas, and provide the basis for the prioritization of streams, components, and classes of materials for further testing by more stringent techniques and procedures. As such, the results of the sampling and of the corresponding analysis procedures should be quantitative within a factor of ±3. A detailed discussion of the approach along with the criteria used for method selection is given in the Methods and Procedures Manual developed for this program. In addition, changes in methods and procedures have occurred during the course of this program to reflect experience, changing data needs, and EPA-directed Level I changes.

TABLE 42. OPERATING LOAD AND ENERGY INPUT RATES OF THE INDUSTRIAL COMBUSTION SOURCES TESTED

Combustion source type	Site No.	Operating load (GJ/hr)	Percent of base load	Energy input (GJ/hr)	Excess air at stack exit (percent)
External Combustion					
Natural Gas	150	15	60	18.5	120
	151	5.4	67	6.8	10
	157	89	50	117	75
	158	4.5	30	5.3	40
	159	50	70	63	50
	161	50	70	63	35
	162	50	70	63	95
	328	27	76	34	50
	334	49	80	61	34
	335	49	80	61	20
Residual Oil	172	35	81	43	25
	153	35	82	43	38
	160	52	67	66	50
	163	37	47	46	20
	202/203				20*
Distillate Oil	170	83	72	104	48
	172	93	60	116	85
	173	39	93	48	75
	174	75	70	94	35
Bituminous, pulverized dry bottom	200/201	93	89	104	20*
	341	205	80	256	61
Bituminous, pulverized wet bottom	223	150	61	167	125
	224	120	65	133	100
	225	120	65	133	55
Bituminous, stoker	221	144	91	179	100
	226	52	40	65	220
	340	123	80	153	125
Wood, underfeed stoker	145	13	100	15.8	100
	146	60	106	76	90
	147	92	95	115	110
	148	35	80	51	140
	149	3.7	20	5.5	450

*Combustion chamber excess air.

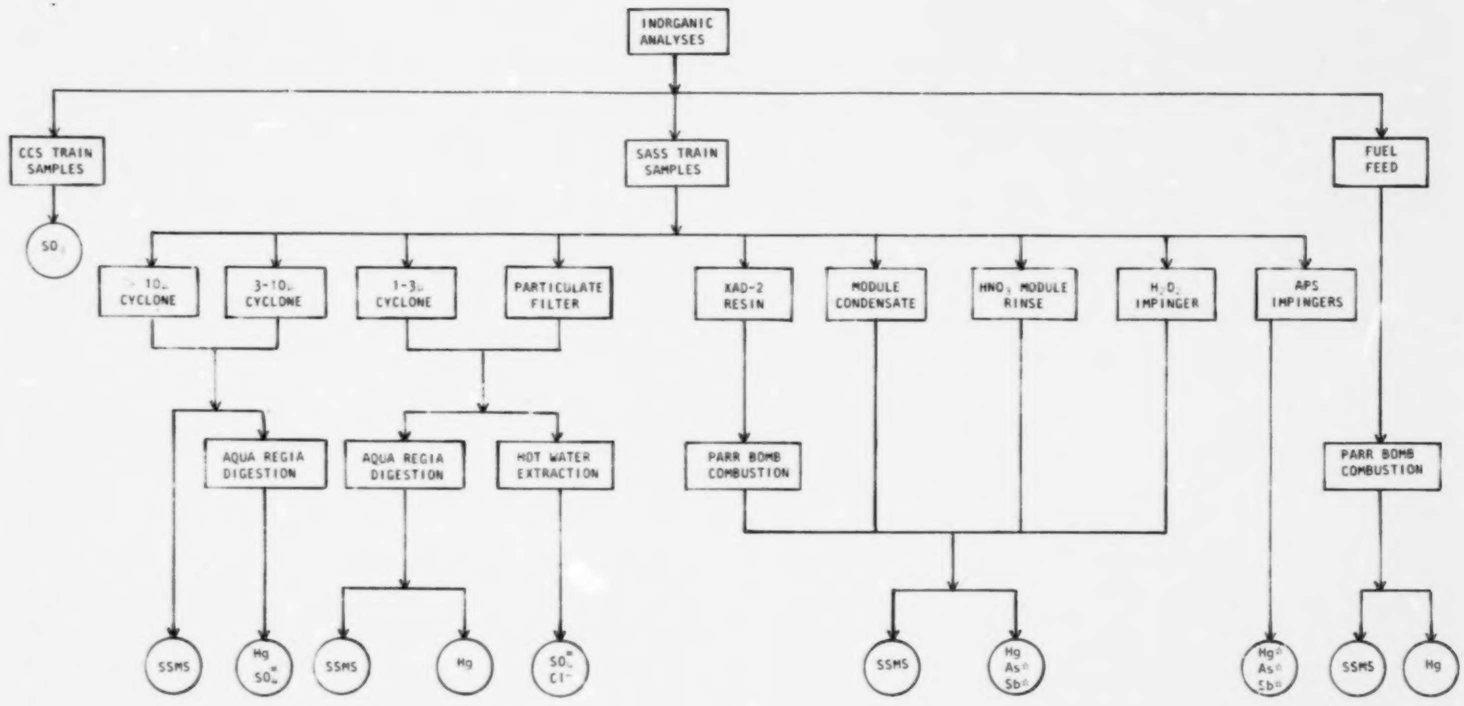
A detailed list of these changes is provided in Volume III of this program series. Major changes include the following:

- The computation of inorganic emissions from gas- and oil-fired sites has been modified, based on the assumption that inorganic emissions are nil from gas-fired sites and that all inorganics from fuel oil combustion are emitted from the stack. Thus, inorganic emissions from oil-fired sites are calculated from analysis of the fuel.
- Organic emission fram gas- and oil-fired sites are integrated values as a result of combination of SASS fractions prior to analysis.
- For solid fuel-fired sites sampled after June 1978, the XAD-2 resin residue (after Parr bomb combustion) was combined with the composite (module condensate, HNO_3 module rinse, and H_2O_2 impinger) sample prior to analysis by SSMS for inorganics.
- AAS analysis of the second and third (APS) impingers for Hg is conducted only if the Hg concentration in the fuel is >1 ppm and "real values" are obtained for the composite sample.
- The NO_x analysis procedure was changed to EPA Method 7 as a result of NO_x loss over time in the Tedlar gas sampling bags.

4.2.3.1 Inorganic Analysis--

As noted above, the inorganic analysis scheme was modified in the case of gas- and oil-fired sites, eliminating inorganic determinations for gas-fired sites and restricting inorganic determinations for oil-fired sites to an analysis of the fuel. In the case of the solid fuel-fired sites, the modified Level I analysis plan shown in Figure 5 was followed. The analytical scheme consisted of an elemental survey by Spark Source Mass Spectrometry (SSMS) for the determination of approximately 70 elements. Specific analyses by Atomic Absorption Spectrometry (AAS) were conducted for mercury and, when indicated by the results of the fuel analysis, for arsenic and antimony. Particulate sulfate was determined turbidimetrically, chlorides were measured by specific ion electrode and/or ion chromatography, and SO_3 was determined by an acid-base titration.

Figure 5 also indicates the procedures followed to prepare samples for analysis. Particulate samples were digested with aqua regia before analysis. However, these samples were analyzed by SSMS directly without


INORGANIC ANALYSES
CCS TRAIN SAMPLES
SASS TRAIN SAMPLES
FUEL FEED
SO₂
> 10μ CYCLONE
3-10μ CYCLONE
1-3μ CYCLONE
PARTICULATE FILTER
XAD-2 RESIN
MODULE CONDENSATE
HNO₃ MODULE RINSE
H₂O₂ IMPINGER
APS IMPINGERS
AQUA REGIA DIGESTION
AQUA REGIA DIGESTION
HOT WATER EXTRACTION
PARR BOMB COMBUSTION
PARR BOMB COMBUSTION
SSMS
Hg SO₄⁼
SSMS
Hg
SO₄⁼ Cl⁻
SSMS
Hg As* Sb*
Hg* As* Sb*
SSMS
Hg

*Analysis dependent on certain criteria.

Figure 5. Modified Level I inorganic analysis plan for industrial solid fuel-fired combustion sources.

preparation whenever possible; i.e., no glass fiber filter material was present. Samples for chloride analysis were extracted with hot water; this extract was also the preferred sample for sulfate analysis. Fuel feeds and XAD-2 resin were prepared by combustion in a Parr oxygen bomb to destroy the organic matrix. No preparative steps were necessary for the other inorganic samples.

Brief descriptions of the analytical techniques used for inorganic characterizations are provided below.

- SSMS - SSMS was used in the laboratory to perform a semi-quantitative elemental survey analysis on all types of Level I samples. The analysis was performed using a JEOL Analytical Instruments, Inc., Model JMS-01BM-2 Mass Spectrograph. The JMS-01BM-2 is a high resolution, double-focusing mass spectrometer with Mattauch-Herzog ion optics and ion sensitive photoplate detection. The instrument is specially designed to carry out high sensitivity trace element analysis of metals, powders, or semiconductor type materials using an RF spark ion source. Elemental analysis by SSMS involves the incorporation of a sample aliquot into two conducting electrodes, which are decomposed and subsequently analyzed by a mass determination using a double-focusing mass spectrometer. Decomposition of the sample electrodes is accomplished by applying a radio frequency (1 MHz) potential of about 4 kV, which induces an electrical discharge in the form of a spark plasma. Because of the high energy associated with the discharge, the spark plasma created is composed primarily of elemental species. The positively charged ions contained in the plasma are accelerated and formed into an ion beam by a high potential electric field (30 kV). The beam is then energy-focused and momentum-dispersed to produce a mass spectrum that is recorded by an ion-sensitive photoplate.

  SSMS can be used to detect elemental species contained in the sample electrodes at levels down to 10^{-9} grams. Although the sensitivity varies somewhat, depending on the element of interest and the sample type, practically all elements in the periodic table can be detected. Using photoplate detection, all elements having masses in the range 6 to 240 can be detected simultaneously. Concentration data are derived from the intensities (optical density) of the mass spectral lines. There are several methods for determining concentration data from photoplate spectral line densities. The methods vary widely in terms of their complexity and corresponding precision and accuracy of the results. The photoplate interpretation procedures followed for this program and for Level I survey work in general are designed to yield concentration data accurate to within a factor of 2 for 70 elements.

- Mercury - Cold Vapor - The cold vapor mercury analysis is based on the reduction of mercury species in acid solution with stannous chloride and the subsequent sparging of elemental mercury, with nitrogen, through a quartz cell where its absorption at 253.7 nm is monitored.

- Arsenic - Hydride Evolution - This procedure entails the reduction and conversion of arsenic to its hydride in acid solution with either stannous chloride and metallic zinc or sodium borohydride. The volatile hydride is swept from the reaction vessel, in a stream of argon, into an argon-hydrogen flame in an AAS. There, the hydride is decomposed and the arsenic concentration is monitored at its resonance wavelength, 193.7 nm. Excess hydrogen peroxide and nitric acid present in certain Level I samples interfere with the analysis and must be removed before the addition of either the zinc slurry or sodium borohydride used to generate the arsenic hydride.

- Antimony - Hydride Evolution - Antimony-containing compounds are decomposed by adding sulfuric and nitric acids and evaporating the sample to fumes of SO_3. The antimony liberated is subsequently reacted with potassium iodide and stannous chloride, and finally with sodium borohydride to form stibine. This stibine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame in an AAS. The gas sample absorption is measured at 217.6 nm. Because stibine is freed from the original sample matrix, interferences in the flame are minimized.

- Sulfate - Turbidimetric - The basis of the analysis is the formation of a barium sulfate precipitate in a hydrochloric acid medium with barium chloride in such a manner as to form barium sulfate crystals of uniform size. The absorbence of the barium sulfate suspension is measured by a transmission photometer and the sulfate ion concentration determined by comparison of the reading with a standard curve.

- Chloride - Specific Ion Electrode and Ion Chromatography - Chloride is determined potentiometrically using a solid state selective ion chloride electrode in conjunction with a double junction reference electrode and a pH meter having an expanded millivolt scale. Ion chromatography is used to check the results of the specific ion electrode determinations, and results are generally in excellent agreement.

- SO_3 - Controlled Condensation - The SO_3 concentration of the Goksoyr-Ross sampling train condenser coil rinse is determined by an acid-base titration against 0.02N sodium hydroxide that has been standardized against primary standard potassium acid phthalate.

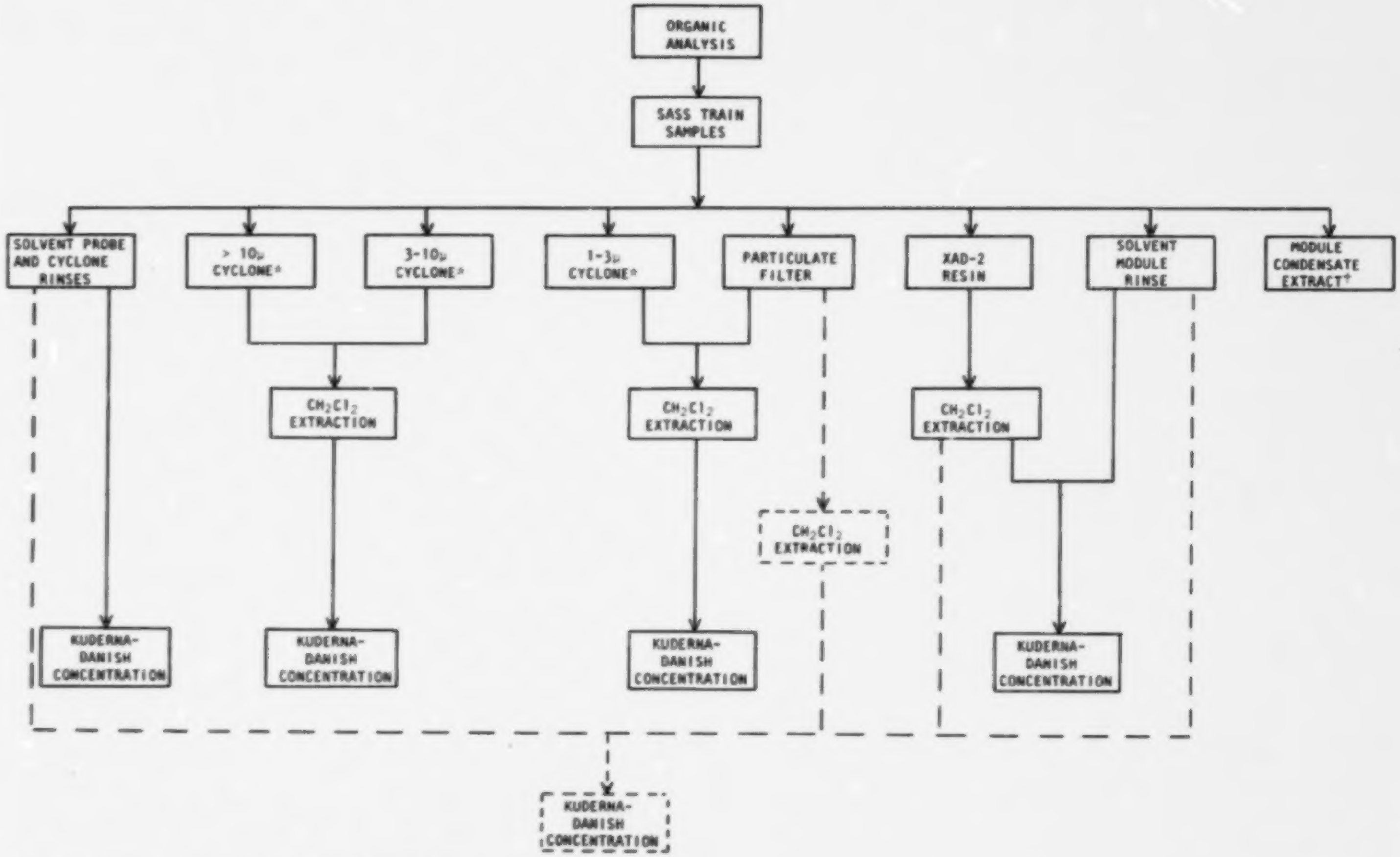
4.2.3.2 Organic Analysis--

An overview of the SASS train samples collected from industrial sources for organic analysis is shown in Figure 6. The sample preparation procedures and appropriate sample combination schemes are also shown in the figure. Organic liquids required no preparation; however, aqueous liquids and solid samples were extracted with methylene chloride to separate the organic and inorganic portions before analysis. In the case of gas- and oil-fired sites, the solvent rinses of SASS train components were combined with the solvent extracts of the XAD-2 resin and particulate filters for concentration into one organic sample for analysis.

The modified Level I organic analysis methodology and decision criteria used for organic characterization of industrial sources are presented in Figure 7. All samples were first concentrated in Kuderna-Danish evaporators to 10-ml volumes. (If material dropped out of solution during concentration, the extract was restored to a convenient volume large enough for the material to redissolve.) Two 1-ml aliquots were taken from each concentrate for the following analyses:

- total chromatographable organic material (GC-TCO) and GC/MS analysis for POM and
- gravimetric determination of nonvolatile organic material and an infrared (IR) analysis on the residue from the gravimetric determination.

The data provided by performing the TCO and the gravimetric analyses were used to make the decision as to the analysis path to be followed for all other determinations. The TCO analysis provided quantitative information on the bulk amount of semivolatile organic material in the boiling range of the C_7 to C_{16} alkanes - 90°C to 300°C. The gravimetric analysis provided quantitative results on the amount of nonvolatile organics in the sample. These two values combined gave an estimate of the total organic content of the sample. Whenever the total organic content of the sample was equivalent to a stack concentration of 500 $\mu g/m^3$ or less, the organic analysis was terminated. Whenever the stack concentration value was greater than 500 $\mu g/m^3$, the direction of the analyses depended on the TCO results.


ORGANIC ANALYSIS
SASS TRAIN SAMPLES
SOLVENT PROBE AND CYCLONE RINSES
> 10μ CYCLONE*
3-10μ CYCLONE*
1-3μ CYCLONE*
PARTICULATE FILTER
XAD-2 RESIN
SOLVENT MODULE RINSE
MODULE CONDENSATE EXTRACT†
CH₂Cl₂ EXTRACTION
CH₂Cl₂ EXTRACTION
CH₂Cl₂ EXTRACTION
CH₂Cl₂ EXTRACTION
KUDERNA-DANISH CONCENTRATION
KUDERNA-DANISH CONCENTRATION
KUDERNA-DANISH CONCENTRATION
KUDERNA-DANISH CONCENTRATION
KUDERNA-DANISH CONCENTRATION

*SASS cyclones used at solid fuel-fired sites only.

†CH_2Cl_2 extraction performed in field; analyses performed on unconcentrated extract.

Figure 6. Modified Level I organic sample preparation scheme for industrial sources. (Dashed lines represent combination of samples from gas- and oil-fired sites.)

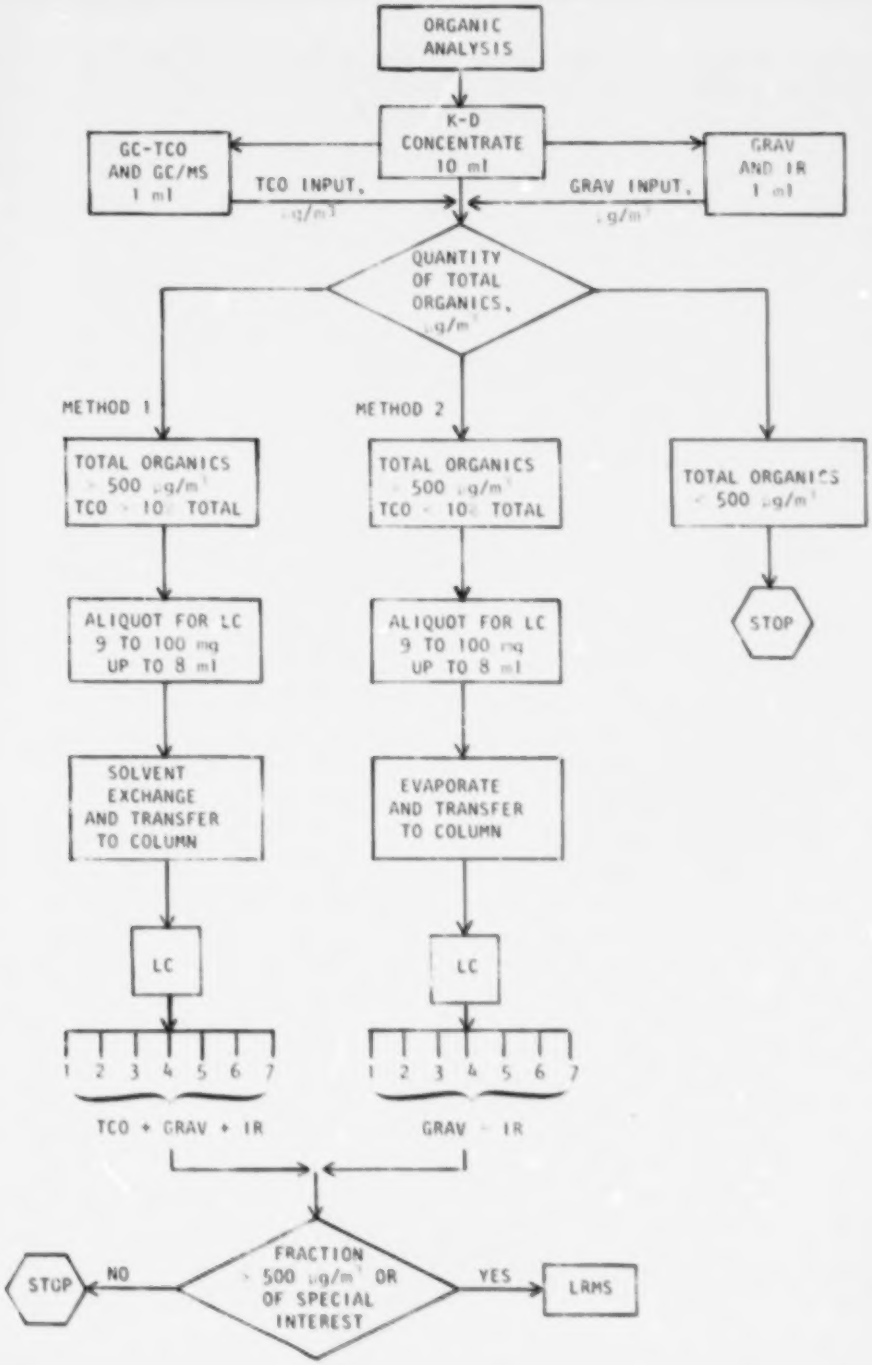

ORGANIC ANALYSIS
K-D CONCENTRATE 10 ml
GC-TCO AND GC/MS 1 ml
GRAV AND IR 1 ml
TCO INPUT, µg/m³
GRAV INPUT, µg/m³
QUANTITY OF TOTAL ORGANICS, µg/m³
METHOD 1
METHOD 2
TOTAL ORGANICS > 500 µg/m³ TCO > 10% TOTAL
TOTAL ORGANICS > 500 µg/m³ TCO < 10% TOTAL
TOTAL ORGANICS < 500 µg/m³
STOP
ALIQUOT FOR LC 9 TO 100 mg UP TO 8 ml
ALIQUOT FOR LC 9 TO 100 mg UP TO 8 ml
SOLVENT EXCHANGE AND TRANSFER TO COLUMN
EVAPORATE AND TRANSFER TO COLUMN
LC
LC
1 2 3 4 5 6 7
1 2 3 4 5 6 7
TCO + GRAV + IR
GRAV + IR
STOP
NO
FRACTION > 500 µg/m³ OR OF SPECIAL INTEREST
YES
LRMS

Figure 7. Modified Level I organic analysis plan for industrial sources.

If the TCO was less than 10 percent of the total organic material, the analytical pathway labeled "Method 2" in Figure 7 was followed. A suitably sized sample aliquot was taken for liquid chromatographic fractionation, evaporated to dryness, and transferred to an LC column. Each separated fraction was subsequently subjected to gravimetric and infrared analyses. If the TCO was greater than 10 percent of the total organics, an aliquot for LC was prepared by solvent exchange to preserve the volatile species. In this "Method 1" procedure, each fraction separated still underwent gravimetric and infrared analyses; however, in addition, these LC fractions were also analyzed for TCO.

The GC-TCO analysis has been used to obtain information on the quantity of material boiling within discrete ranges corresponding to the boiling points of the n-alkanes C_7 through C_{16} as well as on the total amount of material in the overall n-alkane boiling range. Materials were classified solely on the basis of their retention time relative to the n-alkane and were quantitated as n-alkanes. This means any compounds containing oxygen, nitrogen, sulfur, or halogens would also be reported as alkanes.

The infrared analyses provide information on the major functional groups (i.e., chemical compound classes) present in a sample. Data obtained by the GC-TCO and IR analyses are interrelated: many compounds detected in the GC analysis are too volatile to remain when the sample is evaporated for IR analysis; and many compounds identified in the IR analysis have volatilities too low to be detected by the GC-TCO procedure. In a similar manner, the results of GC-TCO analyses of the LC fractions complement the IR analyses of these samples.

Fractions that contained more than 15 mg of material or that were of special interest were analyzed by low resolution mass spectroscopy (LRMS). LRMS is an instrumental technique that may provide molecular weights and compound identification on a "most probable" basis for samples of low complexity. In Level I analysis, it is used to supplement the compound classification derived from IR spectra.

Brief descriptions of the analytical techniques used in conducting the Level I organic analysis and the GC/MS analysis for POM are presented below.

- Extraction of Aqueous Samples - These liquid/liquid extractions were performed with standard separatory funnels. Whenever necessary, the pH of the sample was adjusted to neutral with either a saturated solution of sodium bicarbonate or ammonium chloride. The sample was extracted three times with a volume of high-purity methylene chloride equal to approximately 10 percent of the sample volume. The volume of the resulting extract was measured, dried with anhydrous sodium sulfate, and concentrated to 10 ml.

- Extraction of Solid Samples - The particulate filters, cyclone catches, and XAD-2 resin samples from the SASS train were extracted in appropriately sized soxhlet extractors. Each sample was placed in a glass thimble and extracted for 24 hours with Distilled-in-Glass or Nanograde purity methylene chloride. The resulting extracts were measured, dried, and concentrated.

- Concentration of Organics - The solvent extracts of solid and liquid samples and the solvent rinses of sampling hardware were concentrated in K-D evaporators. Heat provided by a steam bath was sufficient to volatilize the solvents with minimal loss of other organic components. Samples were concentrated to a volume between 5 and 10 ml, allowed to cool, transferred to a volumetric flask, and diluted to a final volume of 10 ml with methylene chloride.

- Gravimetric Determination - The weight of nonvolatile organic species was determined on the concentrates obtained from the K-D concentration of solvent extract and rinse samples. The samples were transferred to tared aluminum weighing dishes, evaporated at ambient temperature, and stored in a desiccator to constant weight. Weights of organic residues as small as 0.1 mg were measured.

- IR Analysis - IR analysis was used to determine the functional groups in an organic sample or LC fraction of a partitioned sample. The interpreted spectra provide information on functionality (e.g., carbonyl, aromatic hydrocarbon, alcohol, amine, aliphatic hydrocarbon, halogenated organic, etc.). Compound identification is possible only when that compound is known to be present as a dominant constituent in the sample.

  The minimum sample amount required for this analysis is 0.5 mg. A compound must be present in the sample at 5 to 10 percent (w/w) at least for the characteristic functional groups of a compound to appear sufficiently strong for interpretation.

Organic solvents, water, and some inorganic materials cause interferences. Water, in particular, decreases the resolution and sensitivity of the analysis.

The initial organic sample concentrate or LC fraction, after evaporation, was either (1) taken up in a small amount of carbon tetrachloride or methylene chloride and transferred to a NaCl window, or (2) mixed with powdered KBr, ground to a fine consistency, and then pressed into a pellet. A grating IR spectrophotometer was used to scan the sample in the IR region from 2.5 to 15 microns.

- TCO Analysis - GC was used to determine the quantity of low boiling hydrocarbons (BP between 90^{o} and $300^{o}C$) in the K-D concentrates of all solvent rinses and organic extracts and in LC fractions 1 through 7 (when the volatile organics were greater than 10 percent of the total organics in the unfractionated sample). Data were used to first determine the total quantity of the lower boiling hydrocarbons in the sample. Whenever this total of C_7 to C_{16} hydrocarbons exceeded a stack concentration of 75 g/m, the TCO results were reported as quantities in each of the C_7 to C_{16} boiling point ranges rather than as a total.

  The extent of compound identification was limited to representing all materials as normal alkanes based on comparison of boiling points. The analysis is semiquantitative because only one hydrocarbon, n-decane, is used for calibration. The differences in instrument response, or sensitivity, to other alkanes are well within the desired accuracy limits for Level I analysis and are not taken into consideration in data interpretation.

- LC Separation - This procedure was designed to separate samples into eight reasonably distinct classes of compounds and was applied to all organic samples that contained a minimum of 500 $\mu g/m^3$ of combined volatile (TCO) and nonvolatile (gravimetric) organics. A sample weighing from 9 to 100 mg was placed on a silica gel liquid chromatographic column, and a series of eight eluents of sequentially increasing polarity was employed to separate the sample into eight fractions for further analyses. Because the use of HCl in the final eluent results in partial degradation of the column material, data were derived from only the first seven fractions.

  Two distinct methods were used to prepare samples for LC fractionation and subsequent analysis. The selection of Method 1 or Method 2 (Figure 4) was based on the results of gravimetric and TCO determinations of the concentrated organic sample. Method 1 was used whenever the volatile organic content determined by the TCO analysis was in excess of 10 percent of the total. Method 2 was used whenever the TCO was low - less than 10 percent of the total.

In Method 1, the low boiling components must be preserved for LC separation and subsequent analysis. This requires a solvent exchange step to transfer the sample from methylene chloride to the nonpolar solvent hexane before placement on the column. In Method 2, where there are few volatile components, a simple, direct solvent evaporation step is sufficient to prepare the sample for fractionation. Gravimetric and IR analyses were performed on the first seven fractions of all LC separations. In addition, whenever Method 1 was used, a TCO analysis was also performed on each of the seven fractions for information on the mass and types of volatile compounds present in each fraction. These data supplement the gravimetric and infrared analyses performed on all fractions.

- LRMS - This procedure is a survey analysis used to determine compound types in an organic sample or in an LC fraction of a sample. The analyst is specifically searching for hazardous compounds or compounds that may be generally considered toxic, e.g., aromatic hydrocarbons and chlorinated organics. Analysis using different sample ionizing parameters results in molecular weight data that, combined with IR and sample source data, can provide specific compound identifications on a "most probable" basis.

  The mass spectrometer (MS) used in this procedure has sufficient sensitivity such that 1 nanogram or less presented to the ionizing chamber results in a full spectrum with a signal ratio of 10:1. A dynamic range of 250,000 is achievable. The detection limit for a specific compound related to the size of an air sample or liquid sample varies widely depending on the types and quantities of the species in the mixture because of interfering effects in the spectrum caused by multiple compounds. The impact of this interference is reduced by lowering the ionization voltage to produce spectra containing relatively more intense molecular ions.

  Solid samples are placed in a sample cup or capillary for introduction through the direct insertion probe. More volatile samples are weighed into a cuvette for introduction through a batch or liquid inlet system. The probe or cuvette is temperature programmed from ambient temperature to 300°C. Periodic MS scans are taken with a 70 eV ionizing voltage as the sample is volatilized during the program. A lower ionizing voltage range (10 to 15 eV) can be used at the discretion of the operator if the 70 eV data are complex. Spectra are interpreted using reference compound spectral libraries, IR data, and other chemical information available on the sample. The results of LRMS analysis give qualitative information on compound types, homologous series, and, in some cases, identification of specific compounds. This information is then used to assess the hazardous nature of the sample.

- Gas Chromatography/Mass Spectrometry Analysis for POM - This is a combined GC/MS method for qualitative and quantitative polycyclic organic material (POM) determinations. Microliter quantities of concentrated sample extracts are used for this analysis.

  Microliter-sized samples are injected onto a gas chromatographic column and are separated by the differences in the retention characteristics between the sample components and the column material. As the components elute from the column, they are transported through an instrument interface to the mass spectrometer (MS), which is being operated in a Total Ion Monitoring (TIM) mode.

  In the MS, the various compounds are ionized, and all ion fragments in the mass range of 40 to 400 amu are monitored. The resulting mass spectra are stored by the computerized data system. All compounds eluting from the GC in detectable quantities could be identified, including aromatic compounds containing heteroatoms, depending on the desired scope of the analysis. The computer is used to search the stored spectra for the specified mass fragments shown in Table 43.

TABLE 43. MASS TO CHARGE (m/e) VALUES MONITORED[a]

128	180	242
154	184	252
162[b]	192	256
166	202	278
178	216	300
179	228	302

[a] Mass to charge values have units in (gm/gm mole)/(electron/molecule).

[b] Internal standard is chloronaphthalene.

The POM spectra are quite distinctive because they yield very strong molecular ions with little fragmentation. Using molecular ions to find POM in a mixture involves reconstructing the GC trace from the stored data using only a single mass to charge (m/e) value. Any inflection in this mass chromatogram indicates the possibility of a POM with that molecular weight. The spectrum is then displayed, and the operator judges if the spectrum is consistent with a POM. The GC retention time and the spectrum are used to make this identification, although it is often difficult to confirm which isomer is causing a peak without standards for the specific material.

Using this technique, a large number of POM can be screened in a short period of time, and good identification of POM type is possible. More time is required for exact identification. Table 44 lists POM that are sought in all samples; any POM with a molecular weight on this list will be determined. If other POM with different molecular weights are desired, all that is needed for their identification is the molecular weight and a relative retention time or a standard. During the search of the data for POM compounds, non-POM compounds may interfere, especially if they coelute with a POM. Computer data interaction techniques, such as ion mapping, keep these interferences to a minimum. If a POM is confirmed, the peak is quantitated using an internal standardization method.

The GC/MS sensitivity varies with several parameters including the type of compound, instrument internal cleanliness, resolution of closely eluting peaks, etc. Under "everyday" operating conditions, 20 nanograms (ng) eluting in a peak about 5 seconds wide yields an MS signal with a usable signal to noise ratio. Typically, this represents at least 100 μg of any single POM compound in a concentrated extract of a sample.

4.2.3.3 Detection Limits--

A minimum flue gas sampling volume of 30 m^3 is required for all SASS runs to ensure that all pollutant species of interest, both inorganic and organic compounds, can be detected at levels that represent the lower limits of environmental concern. A detailed discussion of detection limits of analysis procedures is presented in the program Methods and Procedures Manual.

4.2.4 Test Results

4.2.4.1 Field Measurement Results--

Oxygen concentration data and particulate, NO_X, CO_2, and hydrocarbon flue gas emissions data for the tests conducted are shown in Table 45. The C_1-C_6 gaseous hydrocarbon measurements were conducted in the field, but the C_7-C_{16} and the > C_{16} hydrocarbon emissions were determined in the laboratory. These laboratory determinations are included in Table 45 to facilitate comparison with C_1-C_6 hydrocarbon emissions and calculation of total hydrocarbon emissions.

TABLE 44. MINIMUM LIST OF POM MONITORED

Compound name	Molecular weight	MATE value air ($\mu g/m^3$)
Naphthalene	128	5.0×10^4
Biphenyl	154	1.0×10^3
Fluorene	166	1.4×10^4
Phenanthrene	178	1.59×10^3
Anthracene	178	5.6×10^4
Benzoquinoline	179	N
Acridine	179	9.0×10^4
9,10-Dihydro-phenanthrene	180	N
9,10-dihydro-anthracene	180	N
2-Methyl-fluorene	180	N
1-Methyl-fluorene	180	N
9-Methyl-fluorene	180	N
Dibenzothiophene	182	2.3×10^4
3-Methyl-phenanthrene	192	3.0×10^4
2-Methyl-phenanthrene	192	3.0×10^4
2-Methyl-anthracene	192	30x $\times 10^4$
Ethyl fluorene	195	N
Methyl Dibenzothiophene	196	N
Fluoranthene	202	9.0×10^4
Pyrene	202	2.3×10^5
Dimethyl phenanthrenes	206	N
Benzo (a) fluorene or 1,2-benzofluorene	216	N
Benzo (b) fluorene or 2,3-benzofluorene	216	N
Benzo (c) fluorene or 3,4-benzofluorene	216	N
2-Methyl-fluoranthene	216	N
4-Methyl-pyrene	216	N
3-Methyl-pyrene	216	N
1-Methyl-pyrene	216	N
Trimethyl phenanthrenes	220	N

(continued)

TABLE 44. MINIMUM LIST OF POM MONITORED

Compound name	Molecular weight	MATE value air ($\mu g/m^3$)
Naphthalene	128	5.0 x 10^4
Biphenyl	154	1.0 x 10^3
Fluorene	166	1.4 x 10^4
Phenanthrene	178	1.59 x 10^3
Anthracene	178	5.6 x 10^4
Benzoquinoline	179	N
Acridine	179	9.0 x 10^4
9,10-Dihydro-phenanthrene	180	N
9,10-dihydro-anthracene	180	N
2-Methyl-fluorene	180	N
1-Methyl-fluorene	180	N
9-Methyl-fluorene	180	N
Dibenzothiophene	182	2.3 x 10^4
3-Methyl-phenanthrene	192	3.0 x 10^4
2-Methyl-phenanthrene	192	3.0 x 10^4
2-Methyl-anthracene	192	30x x 10^4
Ethyl fluorene	195	N
Methyl Dibenzothiophene	196	N
Fluoranthene	202	9.0 x 10^4
Pyrene	202	2.3 x 10^5
Dimethyl phenanthrenes	206	N
Benzo (a) fluorene or 1,2-benzofluorene	216	N
Benzo (b) fluorene or 2,3-benzofluorene	216	N
Benzo (c) fluorene or 3,4-benzofluorene	216	N
2-Methyl-fluoranthene	216	N
4-Methyl-pyrene	216	N
3-Methyl-pyrene	216	N
1-Methyl-pyrene	216	N
Trimethyl phenanthrenes	220	N

(continued)

TABLE 44 (continued)

Compound name	Molecular weight	MATE value air ($\mu g/m^3$)
Benzo (c) phenanthrene	228	2.73×10^4
Benzo (ghi) fluoranthene	228	N
Benzo (a) anthracene	228	4.5×10^1
Chrysene	228	2.2×10^3
Triphenylene (9,10-Benzo-Phenanthrene)	228	N
4-Methyl-benzo (a) anthracene	242	N
1-Methyl-chrysene	242	1.79×10^3
6-Methyl-chrysene	242	1.79×10^3
Benzo (f) fluoranthene	252	N
Benzo (k) fluoranthene	252	1.63×10^3
Benzo (b) fluoranthene	252	9.0×10^2
Benzo (a) pyrene	252	2.0×10^{-2}
Benzo (e) pyrene	252	3.04×10^3
Perylene	252	N
Benzo (c) tetraphene	256	N
7,12-Dimethyl-benzo (a) anthracene	256	2.6×10^{-1}
9,10-Dimethyl-benzo (a) anthracene	256	2.96×10^1
1,2,3,4-Dibenzanthracene	278	1.0×10^4
2,3,6,7-Dibenzanthracene	278	N
Benzo (b) chrysene	278	N
Picene	278	2.5×10^3
Coronene	300	N
Benzo (ghi) perylene	302	5.43×10^2
1,2,3,4-Dibenzpyrene	302	N
1,2,4,5-Dibenzpyrene	302	N
Alkyl substituted naphthalenes	-	2.0×10^5
Alkyl substituted biphenyl	-	N

N= Not Available

TABLE 45. FLUE GAS EMISSIONS OF PARTICULATES, NO_x, CO, AND HC FROM THE INDUSTRIAL COMBUSTION SOURCES TESTED

						Hydrocarbons			
Combustion source type	Site No.	O_2 (%)	Particulates (ng/J)	NO_x (ng/J)	CO (ng/J)	C_1-C_6 (ng/J)	C_7-C_{16} (ng/J)	> C_{16} (ng/J)	Total (ng/J)
Gas-Fired Boilers	150	12.0	0.184	-	14	1.7	0.02	0.16	1.88
	151	2.6	0.062	-	337	38.8	0.005	0.09	38.9
	157	9.8	0.09	-	10	0.6	0.03	0.10	0.73
	158	6.8	0.63	-	159	1.8	0.02	0.10	2.02
	159	7.7	0.14	103	2251	0.6	0.06	0.08	0.74
	161	5.9	0.17	81	2058	<2	0.03	0.11	<2.14
	162	11.0	0.15	12	6	0.4	0.03	0.13	0.56
	328	7.9	0.001	51	3	<0.5	0.03	0.25	<0.78
	334	4.7	0.255	-	623	3.3	0.07	0.28	3.65
	335	3.9	0.536	49	165	0.4	0.10	0.68	1.18
Residual Oil-Fired Boilers	152	5.0	8.8	188	5	5.6	0.03	0.07	5.7
	153	6.3	16.4	194	6	6.2	0.05	0.07	6.32
	160	7.7	3.9	146	7	0.1	0.02	0.13	0.25
	163	4.2	3.3	109	6	0.1	0.07	0.09	0.26
	202	5.6	17.6[a]	161	5	<4.6	0.02	0.43	<3.05
Distillate Oil-Fired Boilers	170	7.2	2.4	-	<218	0.1	1.73	1.9	3.73
	172	9.8	19.7	-	<268	0.1	0.02	0.22	0.34
	173	9.3	18.7	-	<506	0.4	0.008	0.12	0.53
	174	6.0	1.0	-	360	0.2	0.03	0.33	0.54
Bituminous, pulverized dry bottom	200	7.9	18.6[a]	372	14	<5.5	0.27	0.33	<6.13
	341	8.0	4.4[a]	-	25	0.42	0.12	1.02	1.56
Bituminous, pulverized wet bottom	223	12.1	10.0[a]	-	0	-	0.08	0.30	0.38
	224	10.9	46.2[a]	-	0	-	0.11	0.58	0.69
	225	7.9	4.0[a]	-	0	-	0.15	0.13	0.28
Bituminous, stoker	221	10.8	20.1[a]	-	0	-	0.33	1.63	1.96
	226	14.8	192[a]	-	0	-	0.05	0.05	0.10
	340	10.4	41[a]	-	61	<0.67	0.33	0.68	<1.68
Wood, underfeed stokers	145	10.4	66.1	67	156	4.2	4.5	7.6	16.3
	146	11.2	18.2	20	257	10.0	0.23	0.20	10.43
	147	10.9	17.5	48	50	0.6	0.04	0.14	0.78
	148	12.2	92	327	ND	0.3	0.04	0.28	0.62
	149	17.5	156	5	1588	73	15.2	121	209.2

[a] After control equipment

- = Not analyzed.

ND = Not detected.

The data represent emissions as measured. However, all of the coal-fired units, two of the wood-fired units and one oil-fired unit were equipped with particulate control devices. These control systems, which include a pilot, double alkali FGD unit on Sites 200 and 202, and their measured or design efficiencies have been listed in Tables 40 and 41. Only a limited number of NO_x emission measurements were made because of the general adequacy of the existing emissions data base for this pollutant. Sulfur dioxide emission data were obtained only at Sites 200 and 202 and the SO_2 removal efficiencies given in Tables 40 and 41 represent actual field data from Reference 15. Sulfur dioxide emissions, however, can be computed for all sites from the fuel sulfur content.

The data reduction procedures for converting emission concentrations (ppm or mg/m^3) to emission factors (ng/J) are presented in Appendix B. The test results presented in Table 45 will be discussed in detail in Section 4.3.

4.2.4.2 Laboratory Analysis Results--

This section presents results of laboratory analyses of samples collected at the combustion sources tested. The analytical methodology used was described in Section 4.2.3.

Inorganic Analysis Results--

Trace element data were obtained by SSMS for the solid fuel-fired sites tested. Results were obtained for up to 65 elements for each section of the SASS train analyzed and were summed to provide a total value and an emission concentration. Emission concentrations for the oil-fired sites were calculated based on fuel analyses assuming that the total elemental content of the fuel is emitted with the flue gas. Trace element analyses were also conducted for the solid fuels. A discussion of the flue gas trace element data will be presented in Section 4.3.

A summary of the data from the specific inorganic analyses conducted is presented in Table 46. Data are shown for emission concentrations of mercury, arsenic, and antimony from oil and coal-fired sources as determined by AAS. The Goksöyr-Ross procedure was used to determine SO_3 concentrations; procedures for the determination of sulfate have been described in Section 4.2.3.

TABLE 46. SUMMARY OF RESULTS OF SPECIFIC INORGANIC ANALYSES FOR THE INDUSTRIAL COMBUSTION SOURCES TESTED

Source category	Site No.	Sample	Emission concentrations ($\mu g/m^3$)				
			Hg	As[a]	Sb[a]	$SO_4^=$[b]	SO_3[c]
Residual oil-fired boilers	152	Fuel	<7.2	-	-	-	-
	153	Fuel	<6.8	-	-	-	-
	160	Fuel	<2.9	-	-	-	-
	163	Fuel	<3.6	-	-	-	-
	202	Flue gas	0.20	-	-	28,000	16,600
Bituminous, pulverized dry-bottom	200	Flue gas	5.0	-	-	19,100	10,400
	341	Flue gas	4.5	0.44	<0.38	3,700	-
Bituminous, pulverized wet-bottom	223	Flue gas	1.70	-	-	-	-
	224	Flue gas	5.41	-	-	6,240	-
	225	Flue gas	3.11	-	-	-	-
Bituminous, stokers	221	Flue gas	3.26	-	-	3,076	-
	226	Flue gas	2.94	-	-	10,460	-
	340	Flue gas	2.07	<0.15	<0.46	5,470	-
Wood, stokers	145	Flue gas	0.40	-	-	6,406	-
	146	Flue gas	0.23	-	-	7,608	-
	147	Flue gas	0.11	-	-	5,534	-
	148	Flue gas	0.58	-	-	4,935	-
	149	Flue gas	0.21	-	-	5,493	-

[a] For SASS sample AI (impinger catch - see Figure 7).

[b] Particulate sulfate.

[c] Flue gas measurement by controlled condensation procedure.

- = not measured.

Organic Analysis Results--

Total Organic Emissions--Tables 47 and 48 present summaries of organic emissions from gas- and oil-fired sites and solid fuel-fired sites, respectively. The data are quantitative and are grouped into three general categories consistent with the procedures used for analysis. These categories are:

- gaseous - compounds boiling below 90°C, C_1-C_6,
- volatile - compounds boiling between 90° and 300°C, C_7-C_{16}, and
- nonvolatile - compounds boiling above 300°C, $> C_{16}$.

Gaseous hydrocarbons are determined in the field, whereas all other organic analyses are performed in the laboratory. The C_1-C_6 field determinations are included here to present an overview of total hydrocarbon emissions.

Large variations exist in total hydrocarbon emissions within all of the source categories tested. Although the data presented in the tables have not been normalized for heat input, the variation is greater than that which could be attributed to differences in excess air or combustion system air leakage. Other factors contributing to the variability, such as system age, fuel, and operating conditions, will be discussed in Section 4.3.

Organic Component Analyses--Further quantitative and qualitative characterizations of organic emissions were conducted in accordance with program procedures as outlined in Section 4.2. The following subsections will discuss the results of these tests.

Liquid chromatographic separation results--As discussed in Section 4.2.3, the composite samples from the gas- and oil-fired sources and the individual SASS component samples from the solid fuel-fired sources are subjected to fractionation into seven components if the total nongaseous organic emissions are found to be greater than 0.5 mg/m^3. Gravimetry and IR spectroscopy are used to analyze each fraction for the amounts of $> C_{16}$ hydrocarbons and compound classes, respectively. If the volatile organic content of a sample exceeds 10 percent of the total organics, then a solvent exchange is performed before the separation to preserve volatile organics, and volatile organics

TABLE 47. TOTAL ORGANIC EMISSIONS FROM THE GAS- AND OIL-FIRED INDUSTRIAL COMBUSTIOM SOURCES TESTED

	Gas-fired boilers										Oil-fired boilers					Distillate oil-fired boilers			
Organics/site	150	151	157	158	159	161	162	328	334	335	152	153	160	163	202	170	172	173	174
Gaseous organics, Field ($\mu g/m^3$)																			
C_1	3,200	147,725	1,730	6,320	1,600	<300	725	<65	7,780	600	17,100	14,731	300	2,320	-	265	200	970	490
C_2	<125	<125	<600	<600	<600	<600	<600	<125	3,090	1,150	0	2,500	<600	<600	-	<125	<125	<125	<125
C_3	<180	<180	<900	<900	<900	<900	<900	<180	<180	<180	0	0	<900	<900	-	<180	<180	<180	<180
C_4	<240	<240	<1,200	<1,200	<1,200	<1,000	<1,200	<240	<240	<240	0	0	<1,200	3,360	-	<240	<240	<240	<240
C_5	<300	<300	<1,500	<1,500	<1,500	<1,500	<1,500	<300	<300	<300	0	0	<1,500	<1,500	-	<300	<300	<300	<300
C_6	<360	<360	<1,800	<1,800	<1,800	<1,800	<1,800	<360	<360	<360	0	0	<1,800	<1,800	-	<360	<360	<360	<360
Total gaseous organics ($\mu g/m^3$)	>3,200	>14,725	>1,730	>6,320	>1,600	<6,300	> 725	<1,270	>10,870	>1,750	17,100	17,230	>300	>5,680	<12,730	>265	>200	>970	>490
Volatile organics, TCO ($\mu g/m^3$)																			
C_7	8	5	6	10	4	8	1	ND	LB	134	9	0	6	2	9	331	16	<1	<1
C_8	21	6	10	0	0	4	0	47	155	95	83	115	4	199	4	613	15	1	<1
C_9	0	0	32	35	155	73	51	LB	LB	3	0	0	17	4	5	894	13	<1	16
C_{10}	0	0	0	0	0	0	0	LB	31	74	1	3	0	0	4	1,760	7	1	3
C_{11}	0	0	3	0	4	4	2	38	LB	LB	0	0	0	6	ND	133	1	4	<1
C_{12}	0	4	5	7	2	3	1	LB	49	15	0	2	2	3	1	330	3	5	15
C_{13}	0	0	4	2	1	1	0	LB	8	19	2	8	4	5	ND	20	3	2	9
C_{14}	0	2	2	1	3	2	0	LB	5	1	1	0	4	5	2	473	2	1	15
C_{15}	0	1	3	2	1	0	0	LB	1	LB	0	0	3	2	1	44	1	1	12
C_{16}	0	0	3	0	0	0	0	LB	LB	4	6	0	8	0	ND	37	2	4	6
Total volatile organics ($\mu g/m^3$)	29	18	68	57	170	95	55	85	249	346	102	128	48	226	26	4,635	68	19	76
Nonvolatile organics, GRAV, $>C_{16}$ ($\mu g/m^3$)	301	346	232	287	230	353	274	665	958	2,380	228	192	321	276	1,200	5,050	484	275	960
Total organics (mg/m^3)	>3.53	>148.1	>2.0	>6.65	>2.0	>0.45	>1.05	>0.75	>12.08	>4.36	17.43	17.55	>0.67	>6.1	>1.22	>9.95	>0.75	>1.27	>1.53

ND = Not detected.

LB = Less than or equal to blank value.

TABLE 48. TOTAL ORGANIC EMISSIONS FROM THE SOLID FUEL-FIRED INDUSTRIAL COMBUSTION SOURCES TESTED

	Bituminous coal								Wood				
	Pulverized dry-bottom		Pulverized wet-bottom			Stokers			Stokers				
Organics/site	200	341	223	224	225	221	226	340	145	146	147	148	149
Gaseous organics, Field (μg/m³)													
C_1	-	830	ND	ND	ND	ND	ND	<65	2,590	17,980	1,930	530	18,700
C_2	-	362	ND	ND	ND	ND	ND	<125	5,230	<600	<600	<600	20,600
C_3	-	<180	ND	ND	ND	ND	ND	<180	<600	<900	<900	<900	3,500
C_4	-	<240	ND	ND	ND	ND	ND	<240	<800	<1,200	<1,200	<1,200	1,450
C_5	-	<300	ND	ND	ND	ND	ND	<300	<1,000	<1,500	<1,500	<1,500	3,900
C_6	-	<360	ND	ND	ND	ND	ND	<360	<1,200	<1,800	<1,800	<1,800	<360
Total gaseous organics (μg/m³)	<13,190	>1,192	ND	ND	ND	ND	ND	<1,270	>7,820	>17,980	>1,930	>530	>48,150
Volatile organics, TCO (μg/m³)													
C_7	-	ND	0	0	0	22	9	92	15	1	2	3	39
C_8	-	10	104	178	358	303	12	71	200	22	0	30	236
C_9	-	243	0	0	0	234	22	67	35	18	0	0	790
C_{10}	-	13	3	11	6	0	4	3	4,810	56	7	8	2,028
C_{11}	-	LB	0	0	0	20	3	382	218	17	5	2	1,876
C_{12}	-	3	0	0	0	3	0	LB	1,774	342	50	10	1,519
C_{13}	-	LB	18	4	3	8	4	0	120	7	2	3	713
C_{14}	-	ND	0	0	0	0	1	2	140	7	1	3	2,560
C_{15}	-	0	2	2	0	0	2	0	1,012	88	3	1	908
C_{16}	-	0	0	2	0	13	3	3	80	3	2	2	195
Total volatile organics (μg/m³)	650	271	127	197	367	603	70	620	8,404	561	72	62	9,931
Nonvolatile organics, GRAV, $>C_{16}$ (μg/m³)	790	2,390	484	1,073	310	2,946	60	1,300	14,305	478	258	463	79,005
Total organics (mg/m³)	>1.44	>3.85	>0.611	>1.27	>0.677	>3.549	>0.66	>1.92	>30.53	>19.02	>2.26	>1.06	>137.1

ND = Not detected.

LB = Less than or equal to blank value.

(TCO) are measured in each fraction. The results of the LC fractionations are presented in Tables 49 and 50 (an explanation of the sample identification codes is given in Figure 8). The results (TCO, GRAV, and total organics) are presented as emission concentrations. However, it should be noted that the concentrations provided in Tables 49 and 50 are generally lower than those previously presented in Tables 47 and 48 because total recovery from the columns is not achieved. In addition, in the case of the solid fuel-fired sources, only data from the XAD-2 resin module or the resin module and condensate are shown. The XAD-2 resin module was designed to trap the bulk of the organic emissions but varying amounts of organics are found in other SASS train component samples.

Examination of the data indicates that the largest amounts of organic materials recovered in the individual fractions are found in LC fractions 6 and 7. The distribution of organics in individual fractions is shown graphically in Figure 9. Fraction 6 should contain in alcohols, phenols, esters, ketones, amines, alkyl sulfur compounds, and some carboxylic acids. Fraction 7 should contain sulfonic acids, sulfoxides, carboxylic acids, and phosphates.

Infrared analysis results--Infrared (IR) spectroscopy was used to determine organic compound classes by functional group analysis in neat sample concentrates and LC fraction residues. Table 51 presents results of the IR analyses of XAD-2 resin samples and LC fractions from the industrial sources tested. Aliphatic hydrocarbons, aromatics, esters, ketones, and carboxylic acids are the compound classes typically found. Benzoates and phthalates are common contaminants, and their presence in the spectra of the samples should be discounted.

Low resolution mass spectral results--As described in Section 4.2.3, low resolution mass spectrometric (LRMS) analysis for compounds and compound classes is performed on any LC fraction of a flue gas sample, the source concentration of which exceeds 0.5 mg/m^3. Table 52 presents results of LRMS analysis of LC fractions meeting this criterion.

TABLE 49. SUMMARY OF LC FRACTIONATIONS FOR THE GAS- AND OIL-FIRED INDUSTRIAL COMBUSTION SOURCES TESTED, mg/m^3

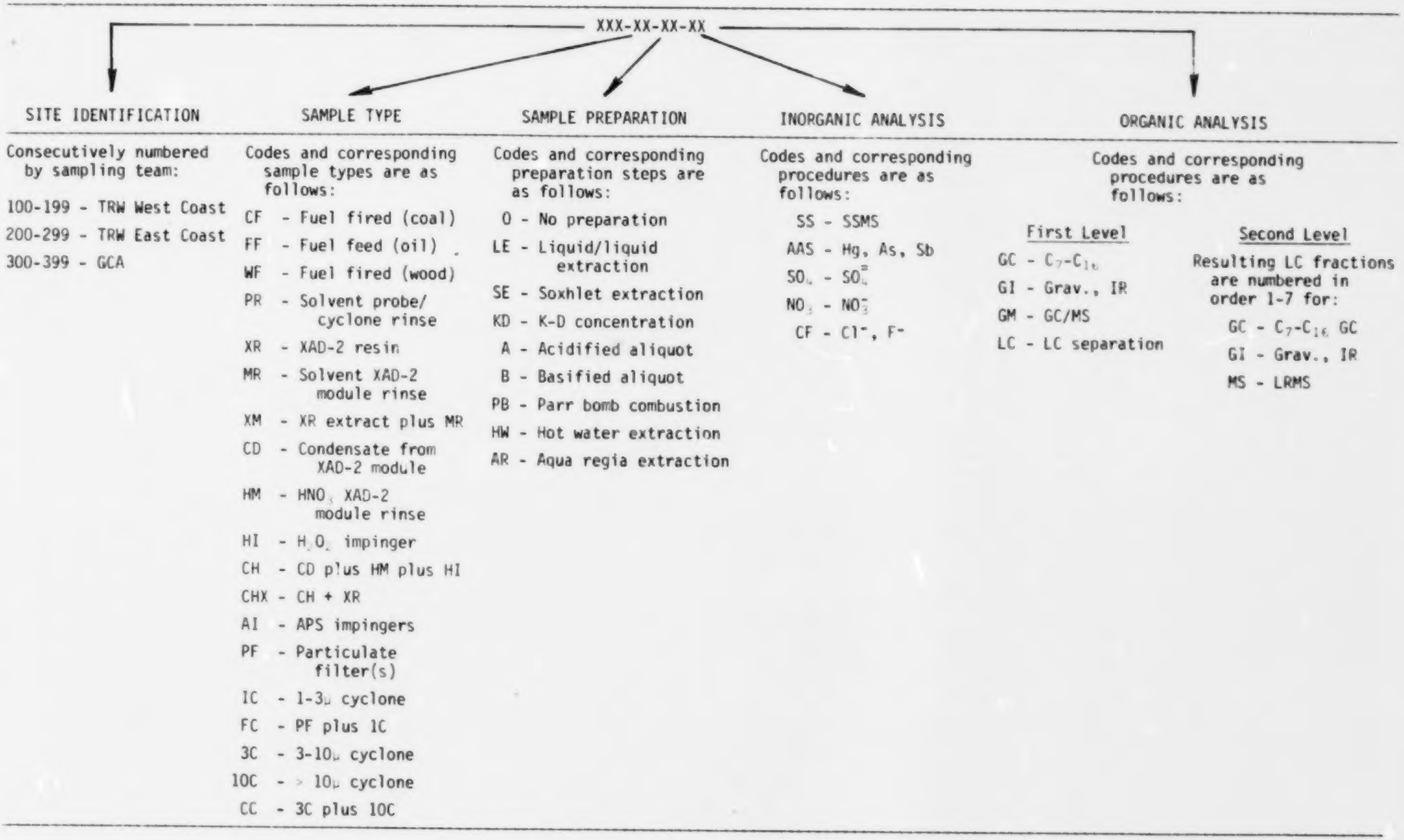
Source category	Site No.	Sample code	Analysis	LC-1	LC-2	LC-3	LC-4	LC-5	LC-6	LC-7	Total
Gas-fired	328	XRPFMRPR	TCO	0.074	<0.001	ND	ND	ND	ND	ND	0.074
			GRAV	0.66	0.009	0.003	ND	0.011	0.11	0.014	0.81
			TOTAL	0.73	0.009	0.003	0	0.011	0.11	0.014	0.88
	334	XRPFMRPR	TCO	ND	<0.001	0.01	0.002	ND	0.002	0.143	0.157
			GRAV	0.12	LB	LB	0.053	0.082	0.202	1.01	1.47
			TOTAL	0.12	<0.001	0.01	0.055	0.082	0.204	1.15	1.63
	335	XRPFMRPR	TCO	0.025	0.004	ND	ND	0.364	0.169	<0.001	0.56
			GRAV	0.118	0.01	0.015	0.06	0.19	0.34	0.63	1.36
			TOTAL	0.143	0.014	0.015	0.06	0.55	0.51	0.63	1.92
Distillate oil-fired	170	XMCDPR	TCO	1.720	0.161	0.340	0.025	0.019	0.495	0	2.760
			GRAV	0.179	0.169	0.105	0.118	0.180	4.328	0.666	5.745
			TOTAL	1.899	0.330	0.445	0.143	0.199	4.823	0.666	8.51
	174	XMCDPR	TCO	0.016	0	0.004	0.041	0.036	0.113	0	0.210
			GRAV	0.051	0	0	0.013	0.051	0.486	0.278	0.879
			TOTAL	0.067	0	0	0.054	0.087	0.599	0.278	1.09

TABLE 50. SUMMARY OF LC FRACTIONATIONS FOR THE SOLID FUEL-FIRED INDUSTRIAL COMBUSTION SOURCES TESTED, mg/m^3

Source category	Site No.	Sample code	Analysis	LC-1	LC-2	LC-3	LC-4	LC-5	LC-6	LC-7	Total
Bituminous, pulverized dry bottom	341		TCO	ND	ND	ND	ND	ND	ND	ND	ND
			GRAV	0.038	0.017	0.030	0.005	LB	LB	0.46	0.551
			TOTAL	0.038	0.017	0.030	0.005	0	0	0.563	0.654
Bituminous, pulverized wet bottom	223	XMCD	TCO	LB	LB	LB	0.003	LB	0.022	0.00	0.025
			GRAV	0.081	0.012	0.018	0.013	0.022	0.272	0.021	0.439
			TOTAL	0.081	0.012	0.018	0.016	0.022	0.294	0.021	0.464
	224	XMCD	TCO	LB	LB	LB	0.012	0.011	0.028	0.011	0.062
			GRAV	0.033	0.003	0.014	0.030	0.049	0.277	0.344	0.750
			TOTAL	0.033	0.003	0.014	0.042	0.060	0.305	0.355	0.812
	225	XMCD	TCO	LB	LB	0.001	0.017	0.005	0.043	0.000	0.066
			GRAV	0.030	0.002	0.010	0.027	0.023	0.179	0.043	0.314
			TOTAL	0.030	0.002	0.011	0.044	0.028	0.222	0.043	0.380
Bituminous stokers	221	XM	TCO	0.060	0.014	0.094	0.322	0.205	0.188	0.008	0.891
			GRAV	0.149	0.017	0.048	0.044	0.112	1.026	0.988	2.384
			TOTAL	0.209	0.031	0.142	0.366	0.317	1.214	0.996	3.275
	226	XMCD	TCO	LB	LB	0.002	0.005	0.010	0.048	0.006	0.071
			GRAV	0.038	0.006	0.015	0.020	0.028	0.183	0.166	0.456
			TOTAL	0.038	0.006	0.017	0.025	0.038	0.231	0.172	0.527
Wood, stokers	145	XM	TCO	2.483	0.058	0.187	0.320	0.188	0.947	0.011	4.195
			GRAV	1.679	0.078	0.693	0.498	0.615	3.088	0.610	7.260
			TOTAL	4.162	0.136	0.880	0.818	0.801	4.035	0.621	11.455
	146	XM	TCO	0.418	0.009	0.004	0.0	0.0	0.006	0.0	0.437
			GRAV	0.041	0.014	0.005	0.010	0.010	0.107	0.073	0.260
			TOTAL	0.459	0.023	0.009	0.010	0.010	0.113	0.073	0.697
	149	XM	TCO	0.229	0.101	0.218	0.278	0.323	0.459	0.0	1.608
			GRAV	1.908	0.128	0.500	0.755	6.367	26.621	5.320	41.599
			TOTAL	2.137	0.229	0.718	1.033	6.790	27.080	5.320	43.207

ND = Not detected.

LB = Lower than Blank Value.



XXX-XX-XX-XX

SITE IDENTIFICATION

Consecutively numbered by sampling team:

100-199 - TRW West Coast

200-299 - TRW East Coast

300-399 - GCA

SAMPLE TYPE

Codes and corresponding sample types are as follows:

CF - Fuel fired (coal)

FF - Fuel feed (oil)

WF - Fuel fired (wood)

PR - Solvent probe/cyclone rinse

XR - XAD-2 resin

MR - Solvent XAD-2 module rinse

XM - XR extract plus MR

CD - Condensate from XAD-2 module

HM - HNO_3 XAD-2 module rinse

HI - H_2O_2 impinger

CH - CD plus HM plus HI

CHX - CH + XR

AI - APS impingers

PF - Particulate filter(s)

IC - 1-3μ cyclone

FC - PF plus IC

3C - 3-10μ cyclone

10C - > 10μ cyclone

CC - 3C plus 10C

SAMPLE PREPARATION

Codes and corresponding preparation steps are as follows:

O - No preparation

LE - Liquid/liquid extraction

SE - Soxhlet extraction

KD - K-D concentration

A - Acidified aliquot

B - Basified aliquot

PB - Parr bomb combustion

HW - Hot water extraction

AR - Aqua regia extraction

INORGANIC ANALYSIS

Codes and corresponding procedures are as follows:

SS - SSMS

AAS - Hg, As, Sb

SO_4 - $SO_4^{=}$

NO_3 - NO_3^-

CF - Cl^-, F^-

ORGANIC ANALYSIS

Codes and corresponding procedures are as follows:

First Level

GC - C_7-C_{16}

GI - Grav., IR

GM - GC/MS

LC - LC separation

Second Level

Resulting LC fractions are numbered in order 1-7 for:

GC - C_7-C_{16} GC

GI - Grav., IR

MS - LRMS

Figure 8. Sample identification and coding for industrial sources.

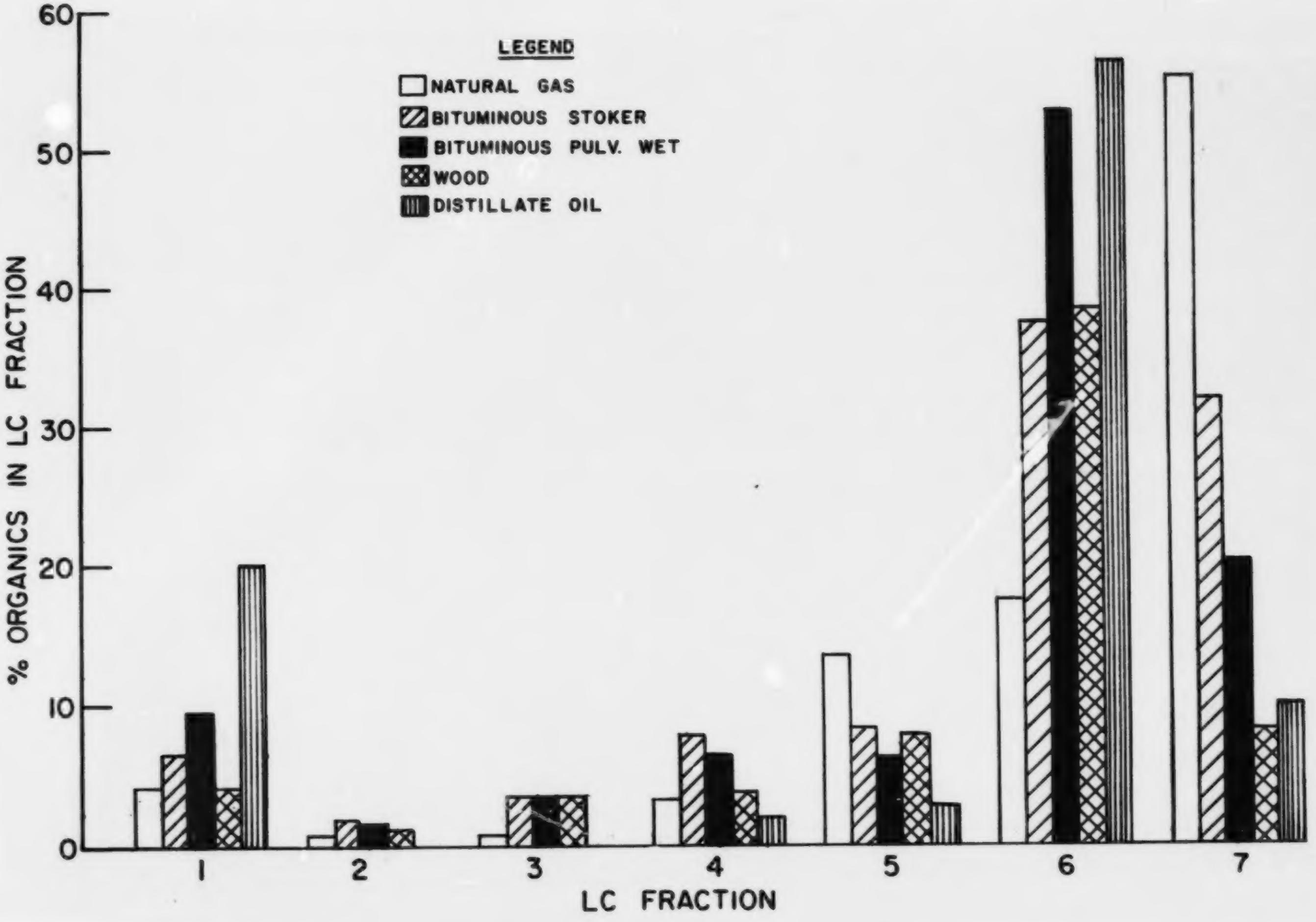


Figure 9. Distribution of organics in LC fractions by source category.

TABLE 51. COMPOUND CLASSES IDENTIFIED BY INFRARED SPECTROMETRY[a]

Site-sample	Original sample	LC-1	LC-2	LC-3	LC-4	LC-5	LC-6	LC-7
Gas-Fired Boilers								
157-XMPCD[b]	Ali, Est, Pnl, Eth	-	-	-	-	-	-	-
158-XMPCD[b]	Est, Eth	-	-	-	-	-	-	-
159-XMPCD[b]	Ali, Est, Pnl, Eth	-	-	-	-	-	-	-
161-XMPCD[b]	Ali, Est, Eth, Pnl	-	-	-	-	-	-	-
162-XMPCD[b]	Ali, Est, Eth, Pnl	-	-	-	-	-	-	-
328-XRPFMRPR	Subst. Ali, Subst. Aro., Aro., Est, Kt (poss), Phth (poss)	Ali Hyd, Aor Hyd, Phth	c	c	c	c	d	c
334-XRPFMRPR	Ali, Aro, CA, Est (poss), Kt (poss), HNC (poss)	c	c	c	c	Aro Est, Pth (poss)	Aro Est, Pth (poss)	Aro, CA, Est (pos
335-XRPFMRPR	Aro, Ali, CA, AM (poss), Est (poss), Kt (poss)	Ali (trace)	Ali, Est, Pth (poss)	c	c	Aro Est, Unsat Est, Sat Kt (poss), Unsat Kt (poss)	Aro CA, Aro Est, AM (poss), Kt (poss), Aol (poss)	Ali CA,
Residual Oil-Fired Boilers								
160-PRXMCD[b]	Est, Eth	-	-	-	-	-	-	
163-PRXMCD[b]	Ali, Est, Eth	-	-	-	-	-	-	
Distillate Oil-Fired Boilers								
170-XMCDPR	Ali, Est, Eth, Aro, A	Ali, Est (trace)	Ali, Est	Ali, Est	Ali, Est, Aro (trace)	Ali, Est, Aro (trace)	Ali, Aro, Est, Eth, A, Pnl (trace)	Ali, Eth
172-XMCDMRPR[b]	Ali, Aro, Est, A (poss)	-	-	-	-	-	-	
173-XMCDMRPR[b]	Ali, Aro, Est, Eth, Pnl, Sl, A (poss)	-	-	-	-	-	-	
174-XMCDPR	Ali, Aro, Est, Eth	Ali, Aro, Est, Pnl	c	c	c	c	A, Ali, Aro, Est, Eth, Pnl	Ali, Aol
Bituminous, pulverized dry bottom boilers								
341-XM	Subst Ali, Aro, Est, CA (poss)	c	c	c	c	c	c	Ca, Ali, Kt (poss) Am (poss)

(continued)

TABLE 51 (continued)

Site-sample	Original sample	LC-1	LC-2	LC-3	LC-4	LC-5	LC-6	LC-7
Bituminous, pulverized wet bottom boilers								
223-XMCD	Ali, Est, Eth (trace)	c	c	c	c	c	Est, Eth	Eth, Est, Ali
224-XMCD	Est, Eth, Aol	Ali	c	c	Est, Ali, Eth	Est, Ali, Eth	Ali, Est, Eth	Aol, Est, Eth,
225-XMCD	Ali, Est, Eth	Ali	c	c	Ali, Est, Eth	c	Est, Eth	Eth, Est
Bituminous, stokers								
221-XM	Ali, Est, Kt, Aro	Ali	c	Ali, Est, Kt, Eth, Fused Aro	Est, Eth	Ali, Est	Aol, Est	Ali, Kt (trace)
226-XMCD	Ali, Est, Eth	Ali	c	c	c	Ali, Est, amine	Ali, Est, Eth	Eth, Est
340-XM	CA, subst. Ali, subst Aro, Kt (poss), Est (poss), Aol (poss)				NO LC			
Wood, stokers								
145-XM	Ali, Est	Ali, Fused Aro	c	Ali, Kt	Ali, Est, Kt	Ali, Kt, Pnl	Ali, Kt, Pnal, unsat	Ali, Kt
146-XM	Est, Eth, Fused Aro	Fused Aro (sub-benzene rings)	c	c	c	c	Est, Eth, Pnl	Eth, Est
147-XM[b]	Est, Eth	-	-	-	-	-	-	-
148-XM[b]	Est, Eth, Fused Aro	-	-	-	-	-	-	-
149-XM	Ali, Est	Ali, trace Kt	c	c	Ali, Est	Est, Kt, Fused Aro	Est, trace Eth	Est, Fused Hyd

[a] All spectra have been blank corrected.

[b] Did not meet criteria for LC-fractionation.

[c] Weight of gravimetric residue did not meet the criteria (>0.5 mg) for IR analysis.

[d] Content of spectra less than that of blank.

Abbreviations used for IR data

A	acids	CS	carboxylic acid salts	Pnl	phenols
Ald	aldehydes	Est	esters	Pth	phthalates
Ali	aliphatic(s)	Eth	ethers	sat	saturated
Am	amides	Gly	glycols	Si	silicones
Aol	Alcohols	HNC	heterocyclic nitrogen compounds	SC	sulfur compounds
Aro	aromatic(s)	Hyd	hydrocarbons	TC	thiocarbonyl compounds
CA	carboxylic acids	Kt	ketones	unsat	unsaturated
Cl	chlorinated hydrocarbons	N	nitro compounds	(tr)	trace
				poss:	possible compounds

TABLE 52. ORGANIC EMISSIONS IDENTIFIED BY LRMS ANALYSIS IN LC FRACTIONS

Site-sample	LC-1	LC-2	LC-3	LC-4	LC-5	LC-6	LC-7
Distillate oil-fired boilers							
170-XMCDPR	a	a	a	a	a	Benzoic acid, carboxylic acids, phthlate esters, naphthalene ring containing materials	Phthlate esters carboxylic acids, sulfonic acids
174-XMCDPR	a	a	a	a	a	Benzoic acid, high MW acids, aromatics	a
Wood-fired boilers							
145-XM	Hyd (sat and unsat)	a	Hys, Si, Pyrene, Phenanthrene	Est, Ald, Kt, Phenanthrene, Pyrene, chrysene	Est, Pnl	Hyd, Pnl	A, Pnl, sulfonic acids
149-XM	Est, Hyd (sat and unsat) Pth, Pyrene, Phenanthrene	a	Aro, Est, Hyd (sat and unsat), Pyrene, Phenanthrene, Si	Aro, Hyd, Methylfluorine, Pyrene, Coronene, C_2 Benzanthracene, Si	Aro, Est, Pnl, Pth, Phenanthrene, Pyrene, Chrysene, Decahydronapthyl-R, Si	Aro, A, Pnl, Si, Dihydroxyphenols	A, AliA, Est, Pth, Si

[a] Did not meet criterion for LRMS analysis.

Abbreviations used for LRMS data

A	acids	CS	carboxylic acid salts	Pnl	phenols
Ald	aldehydes	Est	esters	Pth	phthalates
Ali	aliphatic(s)	Eth	ethers	sat	satuated
Am	amides	Gly	glycols	Si	silicones
Aol	Alcohols	HNC	heterocyclic nitrogen compounds	SC	sulfur compounds
Aro	aromatic(s)	Hyd	hydrocarbons	TC	thiocarbonyl compounds
CA	carboxylic acids	Kt	ketones	unsat	unsaturated
Cl	chlorinated hydrocarbons	N	nitro compounds	(tr)	trace
				poss:	possible

Results of GC/MS analyses for Polycyclic Organic Material (POM)--All organic sample concentrates were analyzed by GC/MS for POM. Table 53 presents the results of POM analyses for the industrial sources. Some compounds shown represent isomers of compounds of identical molecular weight which could not be definitively identified by techniques used for Level I GC/MS analysis. Additional sampling and Level II GC/MS analysis would be required to positively identify compounds emitted from those sources.

TABLE 53. POM EMISSIONS FROM THE INDUSTRIAL COMBUSTION SOURCES TESTED

Source category	Site No.	Sample code	POM compound	Emission concentration ($\mu g/m^3$)
Gas-fired boilers	150	PRFCXM	Naphthalene	11.5
	151	PRFCXM	Naphthalene	19.1
			Phenanthrene	2.7
			Pyrene	1.8
			Fluoranthene	14
	157	PRFCXM	ND	<0.14
	158	PRFCXM	Carbazole	0.96
			Phenanthrene	1.05
			2-methyl phenanthrene	0.17
			Pyrene	1.06
	159	PRXMCD	Biphenyl	3.8
	161	PRXMCD	Biphenyl	0.71
	162	PRXMCD	Biphenyl	6.76
	328	XRMRPR	Naphthalene	7.4
	334	XRPFMRPR	Naphthalene	7.7
	335	XRPFMRPR	Naphthalene	6.0
Residual oil-fired boilers	152	PRFCXM	ND	<0.0008
	153	PRFCXM	ND	<0.0009
	160	PRFCXM	Biphenyl	1.62
	163	PRFCXM	Biphenyl	1.56
	202	XR	ND	-
Distillate oil-fired boilers	170	XMCDPR	ND	-
	172	XMPRCDPR	ND	-
	173	XMPRCDPR	ND	-
	174	XMCDPR	ND	-
Bituminous, pulverized dry bottom	201	XR	ND	-
	341	XMPFCCPR	ND	-

(continued)

TABLE 53 (continued)

Source category	Site No.	Sample code	POM compound	Emission concentration ($\mu g/m^3$)
Bituminous, pulverized wet bottom	223	XMCD	Phenanthrene	0.43
			Pyrene	0.035
	224	XMCD	Biphenyl	0.103
			Dibenzofuran	1.12
			Phenanthrene	3.41
			Dibenzothiophene	0.10
			Pyrene	0.48
	225	PR	Benzo (ghi) perylene	0.003
	225	XMCD	Biphenyl	0.087
			Phenanthrene	0.234
			Pyrene	0.528
			Tetracene	1.878
			Perylene	0.046
			Benzo (ghi) perylene	0.016
Bituminous, stoker	221	FC	None	<0.1
	221	CC	None	<0.1
	221	PR	Naphthalene	0.3
			Phenanthrene	3.8
			Pyrene	2.6
			Fluoranthene	1.9
			Chrysene	0.3
	221	XM	Naphthalene	37
			Phenanthrene	95
			Pyrene	91
			Fluoranthene	30
			Chrysene	53
			Benzo (a) pyrene or Benzo (e) pyrene	7.6
	226	PRCC	Benzo (ghi) perylene	0.057
		XMCD	Phenanthrene	0.672
			O-phenylenepyrene	0.031

(continued)

TABLE 53 (continued)

Source category	Site No.	Sample code	POM compound	Emission concentration (μg/m³)
Wood, stokers	145	PR	Naphthalene	1.3
		FC	Naphthalene	1.3
		CC	Naphthalene	1.3
		CDS	None	<2.5
		XM	Naphthalene	47
	146	PR	Naphthalene	2.0
			Phenanthrene	3.3
			Pyrene	2.0
			Fluoranthrene	2.0
		FC	Naphthalene	3.9
			Pyrene	1.3
		XM	Naphthalene	1244
			Biphenyl	24.5
			Fluorene	7.0
			Phenanthrene	226
			Pyrene	104
			Fluoranthene	174
			Benzo (b) pyrene or Benzo (a) pyrene	8.4
			Benzo (b) fluoranthene	12
			Ideno (1,2,3-C,D) fluoranthene	26
			Benzo (ghi) fluoranthene	15
			(MW = 226)	23
	147	PR	Naphthalene	2.6
	147	FC	Naphthalene	1.3
	147	CC	Naphthalene	2.6
	147	XM	Naphthalene	206
			Biphenyl	1.4
			Phenanthrene	7.0
			Pyrene	2.1
			Fluoranthene	2.8

(continued)

TABLE 53 (continued)

Source category	Site No.	Sample code	POM compound	Emission concentration (μg/m³)
Wood, stokers (continued)	148	PR	ND	<0.00006
	148	FC	Naphthalene	1.3
	148	CC	None	<0.1
	148	XM	Naphthalene	12.4
			Phenanthrene	2.1
			Pyrene	0.7
			Fluoranthene	0.1
	149	PR	ND	<0.00007
	149	FC	ND	<0.0001
	149	CC	ND	<0.0001
	149	CDS	ND	<0.0009
	149	XM	Naphthalene	461
			Biphenyl	38
			Phenanthrene	819
			Pyrene	84
			Fluoranthene	107
			Chrysene	38
			Benzo (e) pyrene or Benzo (a) pyrene	54
			Benzo (b) fluoranthene	69

ND = Not detected.

4.3 ANALYSIS OF DATA EVALUATION AND PROGRAM TEST RESULTS

4.3.1 Emissions of Criteria Pollutants

The particulate, NO_x, CO, and total organic emissions data collected in this program are presented in Tables 54 and 55, respectively, for gas- and oil-fired sources and solid fuel-fired sources. Emissions of SO_2 were not measured in the test program with the exception of tests of a double alkali scrubber at Sites 200/201 and 202/203. (See Reference 15).

4.3.1.1 Gas- and Oil-fired Boilers--

As shown in Table 54 calculated emission factor data variabilities exceed 0.7 for all criteria pollutants from the gas-fired combustion sources tested. Data variability is greatest for the HC and CO emission factors. The variations in emissions of criteria pollutants cannot be completely explained on the basis of boiler load or flue gas oxygen content. As shown in Table 42, all of the boilers, with the exception of those at Sites 150, 151, 157, and 158, were operated at loads greater than 70 percent of rated capacity. Excess air levels measured at the flue gas stack were greater than 25 percent for all boilers except for Site 151 (10 percent), Site 334 (24 percent), and Site 335 (20 percent). The low excess air level and low load operation during testing at Site 151 could explain the high HC and CO emission factors measured at this site. Moderately high HC and CO emission factors were also measured at Sites 334 and 335. However, both of these sites were operated at baseline conditions (80 percent of rated capacity).

The variability of particulate and hydrocarbon emission factors for the residual oil-fired and distillate oil-fired sources tested are greater than 0.7. No definite correlation between boiler operating parameters and emissions of criteria pollutants is apparent, and the variability and level of emissions must be attributed to factors which contribute to combustion efficiency such as fuel atomization, combustion air, and other factors not measured in this program.

TABLE 54. CRITERIA POLLUTANT EMISSION FACTORS AND DATA VARIABILITY FOR THE GAS- AND OIL-FIRED INDUSTRIAL COMBUSTION SOURCES TESTED

Source category	Site number	Emission factor (ng/J)			
		Particulates	NO_x	CO	HC
Gas-fired boilers	150	0.184	-	14	1.9
	151	0.062	-	337	38.9
	157	0.09	-	10	0.7
	158	0.63	-	159	2.0
	159	0.14	103	2051	0.7
	161	0.17	81	2058	<2.1
	162	0.15	12	6	0.6
	328	0.001	51	3	<0.8
	334	0.255	-	623	3.7
	335	0.536	49	165	1.2
	$\overline{X}$	0.22	59	543	5.3
	$S(\overline{X})$	0.07	15	259	3.8
	$tS(\overline{X})/\overline{X}$	0.72	0.71	1.1	1.6
Residual oil-fired boilers	152	8.8	188	4.6	5.7
	153	16.4	194	6.3	6.3
	160	3.9	146	6.9	0.3
	163	3.3	109	5.5	0.3
	202	17.6[a]	161	5.3	<5.1
	$\overline{X}$	8.1	160	5.7	3.5
	$S(\overline{X})$	3.0	15	0.4	1.3
	$tS(\overline{X})/\overline{X}$	1.2	0.26	0.20	1.1
Distillate oil-fired boilers	170	1.4	-	-	3.7
	172	19.7	-	-	0.3
	173	18.7	-	<506	0.5
	174	1.0	-	-	0.5
	$\overline{X}$	10.5	-	-	1.3
	$S(\overline{X})$	5.1	-	-	0.81
	$tS(\overline{X})/\overline{X}$	1.5	-	-	2.0

- = Not measured.

[a] Not included in calculations of mean ($\overline{X}$), standard deviation of the mean ($S(\overline{X})$), or variability ($tS(\overline{X})/\overline{X}$).

4.3.1.2 Solid Fuel-Fired Boilers

Emission factor and variability data, when practicable, are presented in Table 55 for the solid fuel-fired boilers tested. Data variability exceeds 0.7 for all pollutants from all the combustion source categories included in the program. The variability of the particulate emission factor data for bituminous-fired sources has been calculated for uncontrolled emissions only by adjusting the measured emission factors to reflect the design, estimated, or measured efficiency of the control device. All of the bituminous units were controlled by multiclones and/or electrostatic precipitators or, in the case of Site 200, by a double alkali FGD scrubber. The particulate efficiency of this latter unit was determined in the field by actual measurement of inlet and outlet particulate concentrations.

The large variability of the particulate emission factors can be attributed to one or more causes including single-point sampling (stratification of particulates at the sampling location), errors in estimation of control device efficiencies, fuel characteristics and inherent variability in emissions caused by boiler design and operating parameters.

The variabilities of the emission factors for all pollutants from the wood-fired boilers are all relatively high with the exception of that for uncontrolled particulates. However, the variabilities are not too surprising because of the differences in design, operating conditions and fuel burned. The furnaces at Sites 146 and 147 were of dutch oven design; the furnace at Site 149 was a fluid-bed type; and the remaining two units were underfeed stokers. During the test at Site 149 the unit was operating at 20 percent of rated capacity. The poor combustion efficiency of this unit, which contributes in large part to the variability of the pollutant emission data, is reflected by high particulate, CO, and HC emissions and low NO_x emissions.

4.3.1.3 Comparison of Criteria Pollutant Emission Factors

In Table 56, the emission factors for the sources tested in this program are compared with emission factors derived from the existing data base and with EPA emission factors.[9] The mean criteria pollutant factors for most source categories are overall in fair agreement with the existing data base and EPA emission factors. Significant differences in the data bases were most

TABLE 55. CRITERIA POLLUTANT EMISSION FACTORS AND DATA VARIABILITY FOR THE SOLID FUEL-FIRED INDUSTRIAL COMBUSTION SOURCES TESTED

Source category	Site number	Emission factors (ng/J)			
		Particulates	NO_x	CO	HC
Bituminous, pulverized dry bottom boilers	200	18.6	372	14	6.1
	341	4.4	-	25	1.6
	$\bar{X}$	11.5	372	20	3.8
Bituminous, pulverized wet bottom boilers	223	10.0	-	0	0.38
	224	46.2	-	0	0.69
	225	4.0	-	0	0.28
	$\bar{X}$	20	-	0	0.45
	$S(\bar{X})$	13	-	0	0.12
	$ts(\bar{X})/\bar{X}$	2.8	-	0	1.1
Bituminous, spreader stoker	221	20.1	-	0	2.0
	226	192	-	0	0.1
	340	41	-	61	1.7
	$\bar{X}$	84	-	20	1.3
	$S(\bar{X})$	54	-	20	0.6
	$tS(\bar{X})/(\bar{X})$	2.8	-	4.4	1.9
Wood boilers	145	66	67	156	16.3
	146	18	20	257	10.4
	147	18	48	50	0.8
	148	92	327	0	0.6
	149	156	5	1588	209
	$\bar{X}$	70	93	410	47
	$S(\bar{X})$	26	59	297	41
	$tS(\bar{X})/\bar{X}$	1.0	1.8	2.0	2.4

- = Not measured.

TABLE 56. COMPARISON OF CRITERIA POLLUTANT EMISSION FACTORS FOR INDUSTRIAL COMBUSTION SOURCES

Combustion source type	Data source	Emission factor (ng/J)				
		Particulates[a]	NO_x	SO_2[b]	CO	HC
Gas-fired boilers	Current study	0.22	54	ND	543	5.3
	Existing data	2.5	71	3.2	33	6.8
	Combined existing data and current study	1.5	70	3.2	161	6.3
	EPA: AP-42	2-6	50-96	0.26	8	1
Distillate oil-fired boilers	Current study	10.5	ND	ND	ND	1.3
	Existing data	13.7	66	ND	2.1	1.9
	Combined existing data and current study	12.7	66	ND	2.1	1.6
	EPA: AP-42	6	70	106	15	3
Residual oil-fired boilers	Current study	8.1	160	ND	5.7	3.5
	Existing data	39	151	448	3.7	3.0
	Combined existing data and current study	34.5	152	448	4.0	3.2
	EPA: AP-42	30	177	464	15	3
Bituminous, pulverized dry bottom boilers	Current study	196A	372	ND	20	3.8
	Existing data	148A	243	713	ND	3.3
	Combined existing data and current study	160A	261	713	20	3.4
	EPA: AP-42	332A	352	766	20	6
Bituminous, pulverized wet bottom boilers	Current study	110A	ND	ND	0	0.5
	Existing data	ND	ND	ND	ND	ND
	Combined existing data and current study	110A	ND	ND	0	0.5
	EPA: AP-42	251A	586	766	20	6
Bituminous, spreader stokers	Current study	383A	ND	ND	20	1.3
	Existing data	331A	243	ND	132	4.0
	Combined existing data and current study	336A	243	ND	122	2.7
	EPA: AP-42	254A	293	766	40	20
Wood boilers	Current study	135	93	ND	410	47
	Existing data	404	5	ND	ND	ND
	Combined existing data and current study	300	45	ND	410	47
	EPA: AP-42	215-645	430	65	86-2580	86-3010

[a] Indicates fuel ash content.

[b] EPA SO_2 emission factors based on fuel sulfur content of 1.03 percent for bituminous coal and residual oil; 0.24 percent for distillate oil; 0.57 percent for anthracite; and 4,600 g/10^6 Nm^1 for natural gas.

ND - No data

prevalent for CO and HC emissions. Particulate emissions measured in this study also exhibited variations from EPA emission factors, most noticeably for the solid fuel-fired boilers. The particulate emission data reported in Table 56 for the solid fuel-fired sources are uncontrolled emissions and are given, for the bituminous combustion sources, in terms of the ash content of the fuels used during the test program to minimimize possible error in converting measured emissions to uncontrolled emissions. However, other factors, as noted previously, could introduce errors into the conversion from measured to uncontrolled efficiency. Disregarding errors in sampling produced by single-point sampling, the most important factor affecting the calculation of uncontrolled particulate emissions is the control device efficiency. However, those units with the lowest calculated uncontrolled emissions were controlled with multiclones. These units were generally rated at 90 or 95 percent overall efficiency. It is difficult to postulate that these mechanical control units were capable of operating at higher than design efficiencies, a condition that would increase calculated uncontrolled emissions and generally achieve closer agreement with EPA emission factors.

Emission factors for the gas- and oil-fired units were generally in good agreement for particulates and NO_x. The CO emission factor derived from the combined existing data and current study, however, was much higher than the EPA emission factor for gas-fired units and much lower than the EPA emission factor for the oil-fired units. Emissions of CO are highly dependent on unit operations, and the differences in emission factors probably reflect differences in furnace combustion conditions. The hydrocarbon emission factor from the combined data base was much higher than the EPA emission factor for gas-fired units, again probably reflecting differences in furnace design and operation. Hydrocarbon emission factors, however, were in good agreement for the oil-fired sources.

The combined existing data and current study emission factors for wood-fired boilers and EPA emission factors were in fairly good agreement with the exception of NO_x emissions, which were a factor of 10 lower than EPA values. Emissions of HC were also a factor of 2 lower than EPA values.

In summary, the above discussion indicates that (1) the combined existing and current study emission factor data base is generally comparable to the

EPA emission factor data base; (2) the particulate emission data base for solid fuel, coal-fired sources is generally inadequate and will require further study; (3) the NO_x emission data base for wood-fired boilers also requires further study; and (4) the HC and CO emission data base is highly variable and generally inadequate for all combustion source categories.

4.3.1.4 Criteria Pollutant Ambient Severity Factors

The significance of the emissions of criteria pollutants from industrial combustion sources can be assessed using the ambient severity concept. This concept has been discussed in Section 4.1, and detailed methods for the calculation of ambient severity factors are described in Appendix A. Basically, the ambient severity factor is defined as the ratio of the calculated maximum ground-level concentration of the pollutant species to the level at which a potential environmental hazard exists. Ambient source severity factors below 0.05 are deemed insignificant.

Ambient severity factors for the criteria pollutants are presented in Table 57. They have been calculated from the emission factors shown in the table. The emission factors used are best estimates based on analysis of the current study and existing data base for the source categories tested. EPA emission factors are used for many source categories because the combined data from this study and the existing data base are still limited to a comparatively few data points and cannot, as yet, be considered a reliable data base for the estimation of emissions.

Criteria pollutants of potential concern from gas- and oil-fired boilers are NO_x for all sources and SO_2 for residual oil-fired boilers. For bituminous- and wood-fired sources, ambient severities for particulates, NO_x, and SO_2 exceed 0.05 and are significant. Hydrocarbon emissions from bituminous spreader stokers and wood boilers are also significant. The severity factors were calculated for typical industrial size units and represent severity factors for uncontrolled emissions. As indicated in Table 57, pulverized dry bottom units burning bituminous coal at the rate of 200×10^9 J/hr will require control device efficiencies slightly greater than 99 percent to achieve an ambient severity factor of 0.05.

TABLE 57. CRITERIA POLLUTANT EMISSION FACTORS AND AMBIENT SEVERITY FACTORS[a] FOR INDUSTRIAL COMBUSTION SOURCES

	Pollutant									
	Particulates[b]		NO_x		SO_2		CO		HC	
Source category	Emission factor (ng/J)	Ambient severity factor[c]	Emission factor (ng/J)	Ambient severity factor[c]	Emission factor (ng/J)	Ambient severity factor[c]	Emission factor (ng/J)	Ambient severity factor[c]	Emission factor (ng/J)	Ambient severity factor[c]
Gas-fired boilers	2	0.003	70	0.35	0.26	<0.001	8	<0.001	1	0.004
Distillate oil-fired boilers	6	0.009	70	0.35	106	0.11	15	<0.001	3	0.011
Residual oil-fired boilers	30	0.046	170	0.85	464	0.52	15	<0.001	3	0.011
Bituminous, pulverized dry bottom boilers	3320	5.1	350	1.75	766	0.85	20	<0.001	6	0.022
Bituminous, pulverized wet bottom boilers	2540	3.9	586	2.93	766	0.85	20	<0.001	6	0.022
Bituminous, spreader stokers	2540	3.0	290	1.08	766	0.64	40	<0.001	20	0.054
Wood boilers	300	0.46	50	0.25	65	0.072	400	0.007	100	0.36

[a] Based on heat input rates of 200×10^9 J/hr for pulverized units, 150×10^9 J/hr for bituminous spreader stokers, and 50×10^9 J/hr for all other combustion source categories. The sulfur contents used in Table 42 for the calculation of emission factors, and an ash content of 10 percent for bituminous coal.

[b] Uncontrolled emissions

[c] Ambient severity factor values underlined are greater than 0.05.

4.3.2 Particle Size Distribution of Particulate Emissions

Particle size distribution data are based on the weights collected by the three cyclones and the particulate filter of the SASS train during tests of the solid fuel-fired source categories. Emission factors for the size fractions and the percentage of material in each fraction are shown in Table 58. The variability of the percentage in each fraction was also calculated and is shown in the table. The significance of the emission data and data variability is questionable because all of the coal-fired sources and some of the wood-fired sources tested were equipped with control devices. Level II testing upstream and downstream of a control device will be required to adequately estimate emissions and the fractional size efficiencies of specific control devices.

4.3.3 Emissions of Particulate Sulfate, and SO_3

Emission factors and ambient severity factors for particulate sulfate and SO_3 emission are presented in Table 59. The percent of fuel sulfur converted to particulate sulfate or SO_3 is also shown in the table. The SO_3 data was obtained during a study of an industrial boiler burning either residual oil or coal and controlled by a double alkali FGD system.[15] Particulate sulfate emission data were obtained at these two sites in addition to most of the other solid fuel-fired sources tested in this program.

The 3.2 percent conversion of fuel sulfur to particulate sulfate for the single residual oil boiler tested is appreciably greater than the mean value of 0.5 obtained in a previous study.[28] The fuel sulfur conversion to particualte sulfate resulting from the combustion of bituminous coal is highly variable, ranging from 0.12 to 1.6 percent. However, with the exception of the 1.6 percent conversion measured at Site 200, the limited data obtained in this program agree very well with values measured previously for bituminous coal-fired utility boilers. Mean conversion values of 0.032, 0.13, and 0.48 were determined in the Reference 28 study for pulverized dry, pulverized wet, and stoker boilers, respectively. The high percent conversion of fuel sulfur to particulate sulfate during wood combustion is based on an average fuel sulfur content of 0.02 percent. This high percent conversion is very similar to that noted previously in one test of a wood-fired commercial stoker.[39]

TABLE 58. PARTICLE SIZE DISTRIBUTION DATA FOR THE SOLID FUEL-FIRED INDUSTRIAL SOURCES TESTED

Site No.	Control device		Particulate emissions, ng/J (%)				
	Type	Efficiency (%)	>10 µm	3-10 µm	1-3 µ	<1 µm	Total
Bituminous, pulverized dry bottom boilers							
200/201	Double alkali FGD	99.47	0.21(1)	1.5(7)	6.3(30)	13 (62)	21(100)
341	ESP	99	0.5 (13)	1.7(39)	0.7(15)	1.5(33)	4.4(100)
Bituminous, pulverized wet bottom boilers							
223	Multiclone + ESP	99.7	0 (0)	0.6(6)	4.8(48)	4.6(4.6)	10(100)
224	Multiclone	90	3.2 (7)	11.9(26)	22.1(48)	8.8(19)	46(100)
225	Multiclone	95	0 (0)	0.2(1)	1.6(43)	2.2(56)	4(100)
	$\overline{x}$		(2.3)	(11)	(46)	(40)	
	$s(\overline{x})$		(1.3)	(7.6)	(1.7)	(11)	
	$ts(\overline{x})/\overline{x}$		(2.5)	(3.0)	(0.16)	(1.2)	
Bituminous, spreader stokers							
221	Multiclone + ESP	99.5	2.9 (14)	4.8(24)	4.6(23)	7.8(39)	20.1(100)
226	Multiclone	90	2.9 (15)	39 (20)	15 (8)	109(57)	192(100)
340	Multiclone	95	0.8 (2)	6.6(16)	9.6(23)	24 (59)	41(100)
	$\overline{x}$		(10.3)	(20)	(18)	(52)	
	$s(\overline{x})$		(4.2)	(2.3)	(5.0)	(6.6)	
	$ts(\overline{x})/\overline{x}$		(1.7)	(0.5)	(1.2)	(0.53)	
Wood boilers							
145			10.5 (16)	8.3(13)	8.7(13)	38.5(58)	66(100)
146	Scrubber	90	0.3 (1.5)	0 (0)	0.3(1.5)	17.6(97)	18.2(100)
147	Scrubber	90	1.4 (9)	0 (0)	0.4(2)	15.7(89)	17.5(100)
148			14.3 (16)	8.7(9)	8.2(9)	60.8(66)	92(100)
149			43.2 (2.8)	20.8(13)	12.8(8)	79.2(51)	156(100)
	$\overline{x}$		(14)	(7)	(6.7)	(72)	
	$s(\overline{x})$		(4.4)	(2.9)	(2.2)	(8.9)	
	$ts(\overline{x})/\overline{x}$		(0.86)	(1.2)	(0.91)	(0.34)	

TABLE 59. PARTICULATE SULFATE AND SO_3 EMISSION FACTORS AND AMBIENT SEVERITY FACTORS[a] FOR THE INDUSTRIAL COMBUSTION SOURCES TESTED

			Particulate sulfate			SO_3		
Source category	Site No.	Flue gas oxygen (percent)	Percent of fuel sulfur as sulfate	Emission factor (ng/J)	Ambient severity factor	Percent of fuel sulfur as SO_3[b]	Emission factor (ng/J)	Ambient severity factor
Residual oil-fired boilers	302	4.0	3.2	9.1	1.0	0.65	5.7	0.87
Bituminous, pulverized dry bottom boilers	200	8.0	1.6	8.0	0.93	0.40	4.1	0.60
	341	8.0	0.04	1.3	0.15			
Bituminous, pulverized wet bottom boilers	223	12.1	—	—	—			
	224	10.9	0.12	3.2	0.38			
	225	7.9	—	—	—			
Bituminous, spreader stokers	221	10.8	0.15	1.8	0.15			
	226	14.8	1.1	8.8	0.76			
	340	10.4	0.18	2.9	0.25			
Wood boilers	145	10.4	12.6	3.4	0.39			
	146	11.2		3.1	0.36			
	147	10.9		3.0	0.35			
	148	12.2		3.0	0.35			
	149	17.5		3.3	0.38			

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[a] Based on a fuel firing rate of 200 × 10^9 J/hr for pulverized units; 150 × 10^9 J/hr for spreader stokers and 50 × 10^9 J/hr for other combustion source categories.

[b] Based on inlet loadings to scrubber for Sites 200 and 202.

Emissions of SO_3 at Sites 200 and 202 were measured using controlled condensation procedures. The percent conversion of fuel sulfur to SO_3 was 0.40 and 0.65, respectively, for coal and residual oil combustion. The limited existing data base reports corresponding conversions of 0.8 and 1 to 2 percent.

Overall, the emission data for particulate sulfate and SO_3 are highly variable. Moreover, ambient severity factors greater than 0.05 were calculated for all particulate sulfate and SO_3 emissions measured in this program.

4.3.4 Emissions of Trace Elements

Trace element emissions from solid fuel-fired combustion sources were determined from analysis of the collected SASS train samples and emission factors calculated from the SASS data using the techniques described in Appendix B. However, emission factors for oil-fired sources were calculated from analysis of the fuel feed, assuming total release of the elements to the flue gas. Trace element emissions from gas-fired sources were not measured in this program. The SSMS was the principal analytical procedure used for the measurement of trace element emissions, with values for mercury determined by AAS. However, for Sites 200/201 and 202/203, inductively coupled plasma optical emission spectroscopy (ICPOES) analysis was used to determine trace element values. Specific AAS analyses for arsenic and antimony, collected by the APS impingers, were conducted when certain criteria, as described in Section 4.1 were met.

4.3.4.1 Oil-Fired Combustion Sources--

Trace element emission factors, variabilities when possible, and ambient severity factors for the four distillate and residual oil-fired units tested are shown in Table 60. The data variability exceeds 0.7 for all but a few elements, reflecting differences in the trace element content of the fuels and the limited data base. As noted above, the emission factors are based on SSMS analyses of the fuels burned at those sites and on the assumption that all elements exit with the flue gas.

Because of the limited number of data points, variabilities were calculated for only 12 of the 27 elements listed in the table. The ambient severity factors shown in the table were calculated based on the maximum emission factor obtained for the distillate oil-fired sources. In the case of the

TABLE 60. TRACE ELEMENT EMISSION FACTORS AND AMBIENT SEVERITY FACTORS FOR THE OIL-FIRED COMBUSTION SOURCES TESTED

	Distillate oil-fired boilers			Residual oil-fired boilers					
	Site 170/172	Site 173/174		Site 152	Site 153	Site 160/163	Site 201/202		
Trace element	Emission factor (pg/J)	Emission factor (pg/J)	Ambient severity factor[a]	Emission factor (pg/J)	Emission factor (pg/J)	Emission factor (pg/J)	Emission factor (pg/J)	Variability $ts(\overline{x})/\overline{x}$	Ambient severity factor[b]
Aluminum (Al)	175	182	0.004	101	234	195	150	0.54	0.005
Arsenic (As)	2.2	4.8	0.012	LB	LB	1.2	9.4	—	<0.001
Boron (B)	0.09	0.62	<0.001	LB	0.60	LB	12.0	—	<0.001
Barium (Ba)	0.22	2.1	<0.001	3.3	LB	LB	—	—	<0.001
Berylium (Be)	0.02	0.02	0.001	LB	LB	0.02	0.3	—	0.018
Calcium (Ca)	37.7	114	0.006	166	432	88.4	22.0	1.9	0.009
Cadmium (Cd)	LB	1.3	0.003	LB	LB	0.66	21.0	—	0.0051
Cobalt (Co)	0.73	6.8	0.017	13.0	13.2	7.9	3.8	0.65	0.038
Chromium (Cr)	23.8	24.4	0.060	47.4	36.0	4.4	5.7	1.9	0.165
Copper (Cu)	6.7	68.4	0.0008	LB	LB	29.2	2.0	—	0.004
Iron (Fe)	106	661	0.016	LB	25.2	141	88	—	0.0003
Mercury (Hg)	—	—	—	—	—	—	0.1	—	<0.001
Potassium (K)	21.5	148	0.009	190	312	280	—	0.6	0.016
Lithium (Li)	0.04	0.98	0.005	0.24	1.4	0.56	—	2.0	0.014
Magnesium (Mg)	20.7	62.5	<0.001	15.4	32.4	LB	9.4	—	<0.001
Manganese (Mn)	3.0	5.4	<0.001	8.8	14.4	2.0	1.3	1.5	<0.001
Sodium (Na)	60.8	62.5	0.003	853	576	2276	—	1.8	0.17
Nickel (Ni)	44.8	466	0.57	735	1056	393	63	0.63	1.45

(continued)

TABLE 60 (continued)

	Distillate oil-fired boilers			Residual oil-fired boilers					
	Site 170/172	Site 173/174		Site 152	Site 153	Site 160/163	Site 201/202		
Trace element	Emission factor (pg/J)	Emission factor (pg/J)	Ambient severity factor[a]	Emission factor (pg/J)	Emission factor (pg/J)	Emission factor (pg/J)	Emission factor (pg/J)	Variability $ts(\overline{x})/\overline{x}$	Ambient severity factor[b]
Phosphorus (P)	29.5	62.0	0.076	13.0	13.2	26.5	—	1.1	0.045
Lead (Pb)	22.2	25.1	0.020	LB	LB	2.0	4.1	—	0.003
Antimony (Sb)	LB	LB	—	0.12	LB	LB	1.9	—	<0.001
Selenium (Se)	3.3	6.4	0.004	3.9	7.2	0.02	2.0	2.4	0.008
Silicon (Si)	475	994	0.012	16,590	720	LB	0.3	—	0.20
Strontium (Sr)	1.9	4.4	<0.001	3.8	8.6	LB	—	—	<0.001
Uranium (U)	LB	LB	—	LB	LB	LB	—	—	—
Vanadium (V)	1.3	388	0.095	332	648	1.7	260	1.8	0.25
Zinc (Zn)	26.0	58.6	0.002	19.7	80.4	LB	20	—	0.002

[a] Based on the maximum emission factor for each element.

[b] Based on maximum value; upper bound value if variability exceeds 0.7.

— = Not measured.

LB = Lower than blank value.

residual oil-fired sources, either the maximum value or the upper bound of the emission factor was used to calculate severity factors. Data from Site 202 were not included in the calculation of variability or ambient severity factors because this site was controlled by a FGD device. Because of this conservative approach, several elements are associated with ambient severity factors that are greater than 0.05, the level for which emissions are considered environmentally significant in this program. Elements of significance for distillate oil sources include chromium, nickel, phosphorus, and vanadium. For residual oil combustion, elements of significance are cadmium, chromium, sodium, nickel, phosphorus, silicon and vanadium. The data for these elements are inadequate based on the criteria established for this program.

A comparison of current study trace element emission factors with existing data is provided in Table 61. Elements listed are those with high ambient severity factors as determined from the emission factor data in Table 60. The referenced data for distillate oil represent emission factors measured in recent studies of emissions from seven residential and three commercial combustion sources. Because emission factors were also calculated in these studies using trace element fuel concentrations as determined by SSMS, differences between the current study and the existing study data should be directly attributable to the trace element content of the fuels used in the three studies. Reasonable agreement is shown for approximately two-thirds of the 18 elements listed in the table. Emission factors for the remaining elements differ by more than a factor of 3.

In the case of the residual oil-fired sources, the current study data base is compared with data that represent the weighted nationwide trace element content of residual oils[21] and recent trace element emissions data for commercial and utility boilers. Reasonable agreement of the current study data base with the existing data base is shown for 12 of the 18 elements.

In summary, trace element emissions are of concern for several elements emitted from distillate oil-fired combustion sources and residual oil-fired industrial sources. Elements, other than those noted above that are associated with ambient severity factors greater than 0.05, also may be of environmental concern because the range of variability of these elements in oil fuels is unknown.

TABLE 61. COMPARISON OF EXISTING TRACE ELEMENT EMISSION FACTOR DATA WITH RESULTS OF CURRENT STUDY OF OIL-FIRED INDUSTRIAL COMBUSTION SOURCES, pg/J

	Distillate oil-fired boilers			Residual oil-fired boilers			
		Existing data			Existing data		
Element	Current study	Ref. 42	Ref. 43	Current study	Ref. 42	Ref. 21	Ref. 28
Aluminum (Al)	178	15	250	177	156	87	132
Arsenic (As)	3.5	1.3	1.5	1.2	9.1	18	12
Barium (Ba)	1.2	8.4	16	3.3	9.5	29	31
Calcium (Ca)	75	845	450	229	780	320	1428
Cadmium (Cd)	1.3	2.5	11	0.66	0.2	52	6.9
Cobalt (Co)	3.8	2.3	1.0	11	23	50	10
Chromium (Cr)	24	36	29	29	50	30	21
Copper (Cu)	37	205	160	10	93	64	350
Fluorine (F)	—	14	—	—	1.0	2.7	149
Iron (Fe)	383	545	140	83	379	411	453
Mercury (Hg)	—	1.7	1.2	—	1.9	0.9	1.5
Potassium (K)	85	60	230	261	213	777	392
Lithium (Li)	0.5	1.5	1.2	1.1	1.0	1.4	1.7
Magnesium (Mg)	42	40	210	24	111	297	2384
Nickel (Ni)	255	112	290	728	804	964	433
Lead (Pb)	24	48	42	2	7	80	34
Antimony (Sb)	—	1.7	5.7	—	21	10	25
Silicon (Si)	735	173	—	8655	1610	400	595
Vanadium (V)	195	30	2.9	366	250	3656	714
Zinc (Zn)	42	40	110	33	46	29	66

4.3.4.2 Bituminous Coal-Fired Combustion Sources--

As noted previously in Section 4.1, existing trace element emission factor data for industrial solid fuel-fired combustion sources are limited. Further, interpretation of the current study and existing data base is difficult because of the large variations in fuel, control device performance, and other factors related to the combustion source and its operation.

Emission factors and ambient severity factors for the bituminous-fired combustion sources tested in this program are shown in Table 62. The units tested were two pulverized dry bottom units, one controlled by an ESP of an estimated 94 percent efficiency and the other controlled by a double alkali scrubber of 99.47 percent measured particulate efficiency; one pulverized wet bottom unit controlled by a multiclone with an estimated efficiency of 90 percent; and three spreader stokers, two controlled by mechanical precipitators of 90 and 95 percent rated efficiency and one controlled by an ESP rated at 99.5 percent efficiency. The ambient severity factors were calculated from the emission factor data using the heat input rates specified in the table.

Despite the relatively high levels of control at the pulverized dry bottom sites (99.47 and 99 percent, respectively, at Sites 200/201 and 341) the calculated ambient severity factors for some elements are greater than 0.05. These elements are arsenic, beryllium, chromium, and mercury at Site 200/201 and cobalt at Site 341. An ambient severity factors greater than 0.05 at Site 224, a pulverized wet bottom boiler controlled by a multiclone with an estimated efficiency of 90 percent, was found for only one element, phosphorus.

The three bituminous spreader stokers tested were all equipped with control devices. Site 221 was controlled by an ESP with a rated efficiency of 99.5 percent; Site 226 was controlled with a 90 percent rated efficiency multiclone; and Site 340 was controlled with a multiclone with an estimated efficiency of 95 percent. Because of variations in the coal and in the efficiency of the control devices at these sites, the variability of the emission factor was not calculated. Emission factor variability, however, is obviously greater than 70 percent for most elements. Calculated ambient severity factor exceeded 0.05 for beryllium, nickel, and phosphorus at all three sites. Other elements with severity factors greater than 0.05 at one or more of the sites are arsenic, cobalt, chromium, iron, potassium, lithium and lead.

TABLE 62. TRACE ELEMENT EMISSION FACTORS AND AMBIENT SEVERITY FACTORS FOR THE BITUMINOUS-FIRED INDUSTRIAL COMBUSTION SOURCES TESTED

	Bituminous, pulverized dry bottom				Bituminous, pulverized wet bottom				Bituminous, spreader stokers			
	Site 200/201[a]		Site 341[a]		Site 224[a]		Site 221[a]		Site 226[a]		Site 340[a]	
Element	Emission factor (pg/J)	Ambient[b] severity factor	Emission factor (pg/J)	Ambient[b] severity factor	Emission factor (pg/J)	Ambient[b] severity factor	Emission factor (pg/J)	Ambient[b] severity factor	Emission factor (pg/J)	Ambient[b] severity factor	Emission factor (pg/J)	Ambient[b] severity factor
Aluminum (Al)	1100	0.026	761	0.08	1104	0.026	840	0.014	1826	0.032		
Arsenic (As)	92	0.23	6.8	0.017	14.0	0.034	23.1	0.042	44	0.080	367	0.67
Boron (B)	10	<0.001	148	0.005	5.1	0.002	61.5	0.002	44.6	0.001	629	0.019
Barium (Ba)	–	–	21.1	0.005	68.5	0.016	12.7	0.002	158	0.028	26.2	0.005
Beryllium (Be)	1.0	0.061	0.08	0.005	0.09	0.005	1.7	0.078	1.4	0.064	5.2	0.24
Calcium (Ca)	1.5	<0.001	123	<0.001	339	0.001	219	0.001	1552	0.003	682	0.001
Cadmium (Cd)	0.42	0.001	0.21	0.001	0.64	0.002	0.004	<0.001	0.08	<0.001	0.4	<0.001
Cobalt (Co)	5	0.012	35.1	0.085	5.9	0.014	13.4	0.024	11.1	0.020	78.7	0.144
Chromium (Cr)	54	0.13	2.5	0.006	5.3	0.013	7.4	0.018	140	0.34	26.8	0.065
Copper (Cu)	8.4	0.001	34.7	0.004	19.4	0.012	133	0.012	177	0.016	504	0.046
Iron (Fe)	1000	0.024	315	0.008	1410	0.034	595	0.008	2180	0.032	5200	0.073
Mercury (Hg)	37	0.09	1.9	0.005	2.9	0.007	1.8	0.003	2.5	0.005	10.8	0.019
Potassium (K)	–	–	156	0.009	194	0.012	572	0.026	1017	0.047	2518	0.11
Lithium (Li)	–	–	0.89	0.005	0.26	0.001	4.8	0.020	2.0	0.008	33.6	0.14
Magnesium (Mg)	4.6	<0.001	55	0.001	468	0.010	199	0.003	117	0.002	204	0.003
Manganese (Mn)	6.3	<0.001	118	0.003	6.3	<0.001	22.1	<0.001	10.3	<0.001	78.7	0.001
Sodium (Na)	–	–	236	0.011	974	0.048	126	0.005	1370	0.050	1469	0.054
Nickel (Ni)	26	0.021	4.3	0.037	15.6	0.013	440	2.7	13.4	0.08	99	0.60
Phosphorous (P)	–	–	28.3	0.034	88.5	0.11	25.1	0.31	715	0.65	1469	1.3
Lead (Pb)	8.8	0.007	4.6	0.004	10.6	0.009	36.6	0.022	33.6	0.021	310	0.19
Antimony (Sb)	10	0.002	0.46	<0.001	0.52	<0.001	1.6	<0.001	9.1	<0.001	6.8	<0.001
Selenium (Se)	41	0.025	9.7	0.006	0.76	<0.001	2.6	0.012	20.5	0.010	19.4	0.010
Silicon (Si)	–	–	1352	0.016	713	0.009	1509	0.014	1756	0.016	2361	0.022
Strontium (Sr)	24	<0.001	2.9	<0.001	19.2	<0.001	31.5	<0.001	155	0.005	57.7	0.002
Thorium (Th)	–	–	0.97	<0.001	LB	–	0.19	<0.001	2.1	<0.001	0.73	<0.001
Uranium (U)	–	–	0.68	<0.001	1.09	<0.001	0.26	<0.001	2.7	0.002	1.8	0.001
Vanadium (V)	25	0.006	4.6	0.001	4.8	0.001	18.2	0.003	20.4	0.004	46.7	0.009
Zinc (Zn)	20	<0.001	19.0	<0.001	11.2	<0.001	71.2	0.002	13.0	<0.001	68.2	0.002

[a] Controlled boiler: control efficiency is 99.47 percent for FGD scrubber at Site 200/201; 99.5 percent for ESP at Site 221; 95 percent for multiclone at Site 340; and 90 percent for multiclones at Sites 224 and 226.

[b] Based on a heat input rate of 200 × 10^9 J/hr for the pulverized boilers and 150 × 10^9 J/hr for the spreader stokers.

LB = Lower than Blank Value.

– = Not measured.

Although there is an approximate correlation between emission factors and control device efficiency, there are some inconsistencies. Site 340, for example, emits far more elements in significant amounts than are emitted by site 224 despite the rated efficiencies of 95 and 90 percent, respectively. This discrepancy cannot be explained on the basis of EPA emission factors and fuel characteristics, such as ash content.

4.3.4.3 Wood-Fired Combustion Sources--

Trace element emission factors, variabilities of the emission factors, and mean and upper bound ambient severity factors are presented in Table 63 for the wood-fired combustion sources tested. The emission factors shown in the table are measured values. However, the mean value of the emission factor, data variability and the ambient severity factor were calculated for uncontrolled emissions by adjusting the emissions from the controlled boilers at sites 146 and 147 to the uncontrolled level, assuming the control devices were operating at 90 percent efficiency during the test period.

Upper bound ambient severity factors calculated on this basis exceed 0.05 for several elements. These elements are arsenic, calcium, iron, potassium, magnesium, nickel, phosphorus, and lead. The number of elements of potential significance have been increased slightly by including the calculated uncontrolled emission values for sites 146 and 147. However, the high emission factors measured at sites 148 and 149 also contributed significantly to the number of elements with calculated severity factors greater than 0.05. Because of the variability of the data and the large number of elements of potential environmental concern, the trace element data base is inadequate and further work is needed.

4.3.5 Emissions of Organics and POM

The sites tested generally emitted organic compounds at levels lower than would be predicted from EPA emission factors. Analyses of organic emissions from the industrial sources tested indicate that the principal constituents are esters, carboxylic acids, naphthalenes, and aliphatic hydrocarbons. Very few of the source tested emitted organics at levels that met the criterion for LRMS analyses (or LC sample fractions (>500 mg/m^3)). The compounds identified have relatively high MATE values, in the range of 10 to

TABLE 63. TRACE ELEMENT EMISSION FACTORS AND AMBIENT SEVERITY FACTORS[a] FOR THE WOOD-FIRED INDUSTRIAL COMBUSTION SOURCES TESTED

Trace element	Emission factor (pg/J) Site 145	Site 146	Site 147	Site 148	Site 149	Mean[b] $\bar{x}$ (pg/J)	$\frac{ts(\bar{x})}{\bar{x}}$	Mean[b] ambient severity factor	Upper[b] limit ambient severity factor
Aluminum (Al)	470	28.1	50	37.3	1,262	577	0.84	0.013	0.023
Arsenic (As)	1.65	0.97	4.4	0.85	2.5	11.7	1.9	0.029	0.83
Boron (B)	16.2	52.8	1.9	5.4	184	150	1.9	0.002	0.005
Barium (Ba)	49.2	1.3	12.3	133	133	90	0.76	0.021	0.036
Beryllium (Be)	0.012	0.006	1.3	0.002	0.022	0.19	0.15	0.011	0.013
Calcium (Ca)	7930	175	83.6	9,876	51,000	14,280	1.8	0.34	0.95
Cadmium (Cd)	0.50	0.0006	1.4	0.29	0.08	3.0	2.6	0.007	0.025
Cobalt (Co)	0.40	0.085	0.02	0.34	1.3	0.62	0.90	0.002	0.004
Chromium (Cr)	8.0	0.76	11.7	3.6	8.0	6.4	0.81	0.016	0.028
Copper (Cu)	16.5	9.9	13.8	263	14.9	106	1.2	0.012	0.026
Iron (Fe	725	81.5	58.5	278	1,978	876	0.92	0.021	0.040
Potassium (K)	2300	12.4	562	34,400	51,300	18,750	1.5	1.1	2.8
Lithium (Li)	1.8	0.75	0.20	0.70	1.4	2.7	1.3	0.015	0.035
Magnesium (Mg)	1520	167	337	536	4,785	2,370	0.88	0.028	0.052
Manganese (Mn)	228	43.3	22.6	250	431	314	0.42	0.008	0.011
Sodium (Na)	23.6	1.3	27.8	1.3	28.1	66	2.2	0.003	0.010
Nickel (Ni)	4.8	5.3	2.0	2.5	65.0	29	1.2	0.035	0.077
Phosphorus (P)	1047	366	78.4	141	337	1,190	1.5	1.5	3.8
Lead (Pb)	43.2	6.1	12.9	9.4	6.4	49.8	1.2	0.040	0.88
Antimony (Sb)	1.5	0.007	0.35	0.20	0.14	1.1	1.7	<0.001	<0.001
Selenium (Se)	0.35	0.29	0.34	0.46	0.83	1.6	1.1	<0.001	<0.001
Silicon (Si)	420	56	13.8	216	2,429	750	1.6	0.009	0.023
Strontium (Sr)	64.8	4.2	2.8	81.1	145	72	0.78	<0.001	<0.001
Uranium (U)	1.8	1.8	1.8	1.8	1.8	0	0	0	0
Vanadium (V)	1.34	0.45	0.09	0.33	18.3	5.1	1.8	0.001	0.003
Zinc (Zn)	144	233	124	76.9	65.2	770	1.6	0.019	0.049

[a] Based on a heat input rate of 50 x 10^3 J/hr.

[b] Calculated by adjusting emissions from controlled boilers at sites 146 and 147 to the uncontrolled level assuming control devices were operating at 90 percent efficiency.

1000 mg/m^3. Mean ambient severity factors, based on these MATE values, indicate that emissions of organic compounds, excluding POM, from all of the sources tested are not significant. Calculated ambient severity factors are all less than 0.05.

POM emissions from the industrial sources tested have been presented previously in Table 53. POM emission factors and ambient severity factors for the gas, oil, and bituminous combustion sources are shown in Table 64. The variability of the emission factors were not calculated because of the limited number of data points for each POM/source category combination. POM emissions were not significant for the gas, oil, and bituminus, pulverized wet bottom sources at which POM compounds were found. Ambient severity factors for POM emissions from these sources were all less than 0.001, calculated using the maximum POM emission factor for each source category. The POM emissions from bituminous stokers were somewhat greater. Again maximum emission factors, primarily from site 221, were used to calculated the ambient severity factors. Benzo(a)pyrene (BaP) (or its isomer benzo(e)pyrene) was found in the POM emissions from site 221. The calculated ambient severity factor of 192, using the MATE value for benzo(a)pyrene, indicates that POM emissions from the source may be significant. Unfortunately, it was not possible to positively identify benzo(a)pyrene by GC/MS analysis, and Level II analysis would be required to determine the emissions of the benzopyrene isomers. The ambient severity factor shown in the table represents worst-case conditions because it assumes that only benzo(a)pyrene was emitted.

POM emissions factors and associated ambient severity factors for the wood-fired sites are shown in Table 65 along with the variability of the data for the more prevalent POM compounds listed. Data variability exceeded 0.70 for all POM compounds. Two sites, Nos. 146 and 149, emitted several POM compounds including benzo(a)pyrene or its isomer benzo(e)pyrene. Ambient severity factors for benzopyrene were calculated assuming that only benzo(a)-pyrene was emitted and were significant. Phenanthrene was also emitted in significant amounts from site 149.

Because of the possibility that emissions of benzo(a)pyrene from sites 221, 146, and 149 are significant, additional testing is warranted. As noted above, positive identification of this active carcinogen will require

TABLE 64. POM EMISSION FACTORS[a] AND AMBIENT SEVERITY FACTORS[a] FOR THE GAS, OIL, AND BITMUNINOUS COMBUSTION SOURCE CATEGORIES TESTED

		Gas-fired		Residual oil-fired sources		Bituminous, pulv. wet bottom		Bituminous stokers	
POM compound	MATE value (mg/m³)	Maximum emission factor (pg/J)	Ambient severity factor	Maximum emission factor (pg/J)	Ambient severity factor	Maximum emission factor (pg/J)	Ambient severity factor	Maximum emission factor (pg/J)	Ambient severity factor
Naphthalene	50	6.2	<0.001	-	-	-	-	20.4	<0.001
Biphenyl	1.0	3.3	<0.001	0.63	<0.001	0.04	<0.001	-	-
Fluorene	14	-	-	-	-	-	-	-	-
Phenanthrene	1.6	0.7	<0.001	-	-	1.8	<0.001	54.5	0.004
2-Methyl-Phenanthrene	30	0.06	<0.001	-	-	-	-	-	
Fluoranthene	90	3.6	<0.001	-	-	-	-	17.6	<0.001
Pyrene	230	0.47	<0.001	-	-	0.22	<0.001	51.7	<0.001
Chrysene	2.2	-	-	-	-	-	-	29.4	0.002
Naphthalene	0.2[b]	-	-	-	-	0.79	<0.001	-	-
Benzo(g,h i)fluoranthene	0.9[c]	-	-	-	-	-	-	-	-
Benzo(a)pyrene	0.00002	-	-	-	-	-	-	4.2	192[d]
Benzo(b)fluoranthene	0.9	-	-	-	-	-	-	-	-
O-phenylene pyrene	1.6	-	-	-	-	-	-	0.03	<0.001
Benzo(g,h,i)perylene	0.2[b]	-	-	-	-	0.008	<0.001	0.58	<0.001

[a] The maximum emission factor for each POM compound detected within each source category is used to calculate ambient severity factors.

[b] The MATE value for particulate polycyclic aromatic hydrocarbons is used.

[c] The MATE value for benzo(b)fluoranthene is used.

[d] Detected only at site 221; the compound is either benzo(a)pyrene or benzo(e)pyrene.

TABLE 65. POM EMISSION FACTORS AND AMBIENT SEVERITY FACTORS FOR THE WOOD-FIRED COMBUSTION SOURCES TESTED

POM compound	MATE value (mg/m³)	Site No. 145		Site No. 146		Site No. 147		Site No. 148		Site No. 149		Mean emission factor $\bar{X}$	Variability ts($\bar{X}$)/$\bar{X}$
		Emission factor (pg/J)	Ambient severity factor	Emission factor (pg/J)	Ambient severity factor	Emission factor (pg/J)	Ambient severity factor	Emission factor (pg/J)	Ambient severity factor	Emission factor (pg/J)	Ambient severity factor		
Naphthalene	50	27.0	<0.001	512	0.002	112	<0.001	8.3	<0.001	705	0.002	272	1.4
Biphenyl	1.0	-	-	36	0.005	0.75	<0.001	-	-	58	0.007	31.6	2.3
Fluorene	14	-	-	2.9	<0.001	-	-	-	-	-	-	-	-
Phenanthrene	1.6	-	-	94	0.008	3.7	<0.001	1.3	<0.001	1255	0.096	339	2.9
2-Methyl-phenanthene	30	-	-	-	-	-	-	-	-	-	-	-	-
Fluoranthene	90	-	-	72	<0.001	1.5	<0.001	0.06	<0.001	164	<0.001	59	2.1
Pyrene	230	-	-	43	<0.001	-	-	0.43	<0.001	129	<0.001	57	2.9
Chrysene	2.2	-	-	-	-	-	-	-	-	58.	0.003	-	-
Naphthalene	0.2[a]	-	-	-	-	-	-	-	-	-	-	-	-
Benzo(g,h,i)fluoranthene	0.9[b]	-	-	6.2	<0.001	-	-	-	-	-	-	-	-
Benzo(a)pyrene	0.00002	-	-	3.5	209[c]	-	-	-	-	83	5046[c]	-	-
Benzo(b)fluoranthene	0.9	-	-	4.9	<0.001	-	-	-	-	106	0.014	-	-
O-Phenylene pyrene	1.6	-	-	-	-	-	-	-	-	-	-	-	-
Benzo(g,h,i)perylene	0.2	-	-	-	-	-	-	-	-	-	-	-	-
Indeno(1,2,3-c,d)-fluoranthene	0.2[a]	-	-	8.3	0.004	-	-	-	-	-	-	-	-

[a] The MATE value for particulate polycyclic aromatic hydrocarbon is used.

[b] The MATE value for benzo(b)fluoranthene is used.

[c] The compound is either benzo(a)pyrene or benzo(e)pyrene.

Level II GC/MS analysis. Further study of POM emissions from wood-fired sites is definitely needed.

4.3.6 Solid Wastes from Wood-Fired Combustion Sources

Flyash and bottom ash are the principal wastes generated by wood-fired industrial combustion sources. It was estimated that 80×10^9 g of flyash and 160×10^9 g of bottom ash were produced in 1978 assuming 50 percent application of control and an equal distribution of flyash and bottom ash. Although wood combustion is not extensively practiced and the quantities of ash produced are relatively small when compared to the ash produced by coal combustion, the local environmental significance of wood waste disposal is unknown. To add to the limited data base for these wastes, several samples of ash were collected during the tests of the wood-fired sources. These samples were analyzed for trace elements and organics following the program procedures used to characterize the solid samples collected from the flue gas.

The ratio of the pollutant concentration to MATE value (health) for land disposal of solid wastes, instead of the ambient severity factor, is used as an indicator of environmental significance because of the difficulties involved in applying the concept of the severity factor to solid waste discharges. For solid wastes, the severity factor is defined as follows:

$$S = \frac{S_G\, f_1\, f_2}{V_R\, D}$$

where S_G = solid waste generation, g/sec
f_1 = fraction of the solid waste to water
f_2 = fraction of the material in the solid waste
V_R = river flow rate, m^3/s
D = drinking water standard, g/m^3

Of the parameters listed above, the leaching characteristics of most solid wastes are not well known, the river flow rate is highly site dependent, and there is no established drinking water standard for all but a few pollutants. Thus, the use of severity factors in the evaluation of solid waste emission data becomes impractical.

4.3.6.1 Solid Waste Data Acquisition--

To initiate a data base, a selected number of solid waste streams were sampled and analyzed in this program. Solid waste samples were taken from four of the five wood-fired sites sampled. The solid waste streams collected consist of the following:

- Bottom ash - Site 145
- Cinder ash - Site 146
- Bottom ash - Site 146
- Bottom ash - Site 147
- Cinder ash - Site 147
- Scrubber ash - Site 147
- Cinder ash - Site 148

Samples of solid wastes were dried and desiccated upon receipt. Typically, 100-gram aliquots were weighed for soxhlet extraction for organic analysis. One-gram samples were used for SSMS analysis of trace elements.

4.3.6.2 Analysis of Test Results--

4.3.6.2.1 Trace Element Analysis--Elemental analyses of the solid waste samples are presented in Table 66. The data have been grouped into three types of ash: bottom ash, cinder ash, which is ash deposited between the combustion chamber and the stack, and ash captured by the scrubber at Site 147. Data variability has been calculated for the three samples of bottom ash and cinder ash collected. Data variability exceeds 0.7 for all but a few elements. The high variabilities are attributable to the size of the data base but reflect also differences in elemental composition of the wood feed and unit design and operating parameters.

A comparison of mean elemental concentrations in the three types of ash with elemental MATE (or the identical DMEG) values (health) for solid waste is presented in Table 67. Discharge severity, the ratio of elemental concentration to MATE value, is the criterion used to evaluate the significance of ash generated. A discharge severity exceeding one is considered to warrant

TABLE 66. SUMMARY OF TRACE ELEMENT DATA FOR ASH COLLECTED FROM WOOD-FIRED COMBUSTION SOURCES

Trace element	Concentration in bottom ash (ppm)				Variability ts(X)/X̄	Concentration of cinder ash (pp				Variability ts(X)/X̄	Concentration in scrubber ash (ppm)
	Site 145	Site 146	Site 147	Mean X̄		Site 146	Site 147	Site 148	Mean X		Site 147
Al	4,800	15,000	14,000	11,270	1.2	9,000	1,100	19,000	9,700	2.3	8,900
As	17	7.3	4.3	9.5	1.7	8.5	190	8.5	69	3.8	18
B	240	210	59	170	1.4	250	330	240	270	0.44	1,000
Ba	17	3,100	1,800	1,640	2.3	1,800	3,000	3,600	2,800	0.81	560
Be	0.23	0.20	0.57	0.33	1.5	0.11	LB	0.11	0.07	2.1	0.47
Ca	110,000	190,000	56,000	119,000	1.4	840,000	300,000	110,000	416,670	2.7	110,000
Cd	0.18	0.26	0.37	0.27	0.88	0.15	2.1	0.72	1.0	2.5	LB
Co	22	19	11	17.2	0.81	22	7.1	15	14.7	1.3	11
Cr	130	6,700	63	2,300	4.1	31	21	31	27.7	0.52	260
Cu	180	160	46	129	1.4	180	480	180	180	1.5	90
Fe	15,000	52,000	31,000	32,670	1.4	60,100	20,000	61,000	47,030	1.2	22,000
K	6,600	50,000	29,000	28,530	1.9	58,000	28,000	29,000	38,330	1.1	14,000
Li	13	2.9	1.7	5.9	2.6	6.7	8.8	0.8	5.4	1.9	6.9
Mg	LB	40,000	6,300	15,430	3.5	12,000	12,000	6,200	10,070	0.83	12,000
Mn	2,700	19,000	6,000	9,230	2.3	6,000	5,700	3,000	4,900	0.84	5,600
Na	LB	3,900	9,100	4,330	2.6	32,000	2,100	2,200	12,100	3.5	4,200
Ni	260	230	66	185	1.4	66	87	130	94	0.86	140
P	3,300	12,000	14,000	9,770	1.4	13,000	3,200	670	5,620	2.5	6,200
Pb	56	6.3	6.9	23.0	3.1	28	73	55	52	1.1	30
Sb	5.1	4.2	1.3	3.6	1.4	1.3	32	2.6	12	3.6	1.3
Si	24,000	140,000	110,000	91,330	1.6	200,000	12,000	210,000	140,670	2.0	75,000
Sr	1,100	3,800	1,100	2,000	1.9	1,100	1,500	2,200	1,600	0.86	1,100
Th	3.8	3.3	7.2	4.8	1.1	1.9	LB	3.8	1.9	2.5	LB
U	LB	1.2	LB	0.4	4.3	LB	LB	1.3	0.43	4.3	LB
V	64	110	33	69	1.4	66	21	130	72	1.9	65
Zn	86	39	180	102	1.7	180	940	260	460	2.3	350

LB = Lower than blank value.

TABLE 67. DISCHARGE SEVERITY[a] OF TRACE ELEMENTS IN ASH FROM WOOD-FIRED COMBUSTION SOURCES

Trace element	MATE or DMEG health	Concentration in bottom ash (ppm)	Discharge severity	Concentration in cinder ash (ppm)	Discharge severity	Concentration in scrubber ash	Discharge severity[b]
Aluminum (Al)	16,000	11,270	0.70	9,700	0.61	8,902	0.56
Arsenic (As)	50	9.5	0.19	69	1.38	18	0.36
Boron (B)	9,300	170	0.02	270	0.03	1,000	0.11
Barium (Ba)	1,000	1,640	1.6	2,800	2.8	560	0.56
Beryllium (Be)	6	0.33	0.06	0.07	0.01	0.47	0.08
Calcium (Ca)	48,000	119,000	2.5	416,670	8.7	110,000	2.3
Cadmium (Cd)	10	0.27	0.03	1.0	0.10	<0.01	<0.01
Cobalt (Co)	150	17.2	0.12	14.7	0.10	22	0.15
Chromium (Cr)	50	2,300	46	27.7	0.55	260	5.2
Copper (Cu)	1,000	129	0.13	280	0.28	90	0.009
Iron (Fe)	300	32,670	109	47,030	157	22,000	73
Potassium (K)	4,200	28,530	6.8	38,330	9.1	14,000	3.3
Lithium (Li)	70	5.9	0.08	5.4	0.08	6.9	0.10
Magnesium (Mg)	18,000	15,320	0.86	10,070	0.56	12,000	0.67
Manganese (Mn)	50	9,230	185	4,900	98	5,600	112
Sodium (Na)	160,000	4,330	0.03	12,100	0.08	4,200	0.03
Nickel (Ni)	45	185	4.1	94	2.1	140	3.1
Phosphorus (P)	3,000	9,770	3.3	5,620	1.9	6,200	3.1
Lead (Pb)	50	23	0.46	52	1.0	30	0.60
Antimony (Sn)	1 500	3.6	<0.01	12	<0.01	1.3	<0.01
Silicon (Si)	30,000	91,330	3.0	140,670	4.7	75,000	2.5
Strontium (Sr)	9,200	2,000	0.22	1,600	0.17	1,100	0.12
Thorium (Th)	130	4.8	0.04	1.9	0.01	<0.01	<0.01
Uranium (U)	12,000	0.4	<0.01	0.43	<0.01	<0.01	<0.01
Vanadium (V)	500	69	0.14	72	0.14	65	0.3
Zinc (Zn)	5,000	102	0.02	460	0.09	350	0.007

[a] Discharge severity is defined as the ratio of mean elemental concentration to MATE (DMEG) value.

[b] Concentration based on a single data point.

concern regarding impact on health. Bottom ash elements present in concentrations that exceeded MATE values are barium, calcium, chromium, iron, potassium, manganese, nickel, phosphorus, and silicon. Elements in cinder ash at concentrations in excess of the MATE value are arsenic, barium, calcium, iron, potassium, manganese, nickel, phosphorus, lead, and silicon. Elements found in the single scrubber ash samples collected at concentrations greater than their MATE values are calcium, chromium, iron, potassium, manganese, nickel, phosphorus, and silicon.

On the basis of data variability and discharge severity, the trace element data base for ash is inadequate for the 11 elements listed above with respect to health considerations. If ecological effects are considered, other elements of environmental concern are: aluminum, cadmium, vanadium, and zinc. The trace element data base for ash from wood combustion is also inadequate for these elements. Note that because bottom ash, cinder ash, and flyash will be generally combined for disposal, analysis of wood feed will provide adequate characterization of most of the inorganic components of the total ash generated.

4.3.6.2.2 Organic analysis--The ash samples collected were analyzed for TCO and nonvolatile organics. The data are shown in Table 68. As expected, the concentrations of organics in the bottom ash are generally lower than the cinder ash and the one sample of scrubber ash tested. However, the variability of the data is high and it is difficult to make further generalizations. The presence of TCO compounds in the bottom ash is somewhat unexpected because these compounds should vaporize from the ash at combustion chamber temperatures. The maximum TCO concentration found in any of the samples was 97 ppm. This concentration is appreciably less than the MATE values of >11,000 ppm, based on health, for alkanes, alkenes and alkynes of similar carbon number.

The samples were further analyzed for POM by GC/MS. With the exception of naphthalene, which was found in the cinder ash sample from site 147, no POM compounds were found in other samples of cinder and bottom ash. The naphthalene concentration was 2 ppm, well below the MATE value for health of 150,000 ppm for naphthalene. POM compounds were found in the sample of scrubber ash from site 147. POM compounds from this ash, their concentrations and MATE values for the compounds found are presented in Table 69. The compounds identified were the same as those found in the SASS train

TABLE 68. TCO AND GRAVIMETRIC ORGANIC DATA FOR ASH FROM WOOD-FIRED COMBUSTION SOURCES

Site-sample	TCO (μg/kg)											GRAV (μg/kg)	Total organics (mg/kg)
	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	Total		
145-Bottom ash	85	3943	180	1408	1608	38	0	0	0	0	7262	19000	26.262
146-Bottom ash	0	6696	0	0	0	0	0	0	0	0	6696	0	6.696
147-16-Bottom ash	1045	3438	0	0	0	0	0	0	0	0	4483	0	4.483
146-Cinder ash	0	3943	180	1410	1607	38	0	0	0	0	7178	19000	26.178
147-Cinder ash	994	32499	6426	7182	6493	34703.	1880	1780	4751	574	97282.	177904.	275.186
148-Cinder ash	0	7060	0	0	0	0	0	0	200	0	7260	94000	101.260
147-Scrubber ash	5905	9581	0	0	0	0	215	405	0	85	16191	19000	35.191

catch at this site in approximately the same proportions (see Table 65). The concentrations of the compounds identified are well below MATE values. However, the data base for POM from flyash collected from wood-fired sources must be considered inadequate on the basis of POM emissions found in the stack gases of some of the other wood-fired sites tested. These emissions from other sites (146 and 149) included a compound that could be benzo(a)pyrene. If this compound could be positively identified and was found in amounts exceeding its health MATE value of 0.06 ppm, then the disposal of flyash collected from wood-fired sites would pose a hazard to health. Bottom ash disposal does not appear to present a problem.

TABLE 69. POM IDENTIFIED IN SCRUBBER ASH FROM WOOD-FIRED SITE 147

POM compound	Concentration (ppm)	MATE (health) (ppm)
Naphthalene	306	150,000
Biphenyl	3.8	3,000
Phenanthrene	10.5	4,800
Pyrene	1.9	695,000
Fluoranthene	5.7	285,000

5.0 TOTAL EMISSIONS

Based on the results of program sampling and analysis efforts and the existing emissions data base, estimates of current national emissions and projected 1985 national emissions from industrial combustion sources have been made using current and predicted fuel consumption rates.

5.1 CURRENT AND FUTURE FUEL CONSUMPTION

Fuel consumption data for 1978 for the industrial sector were obtained from DOE energy data and EPA report publications. Information provided by these sources was synthesized to obtain fuel consumption estimates presented in Table 70 for the source categories studied in this program. In 1978 the industrial sector consumed about 25 percent of the fuel used by stationary combustion sources. In 1978, 65 percent of the fuel consumed by the industrial sector was natural gas, 4 percent was distillate oil, and 11 percent was residual oil. Solid fuel consumption accounted for the remaining 20 percent, 16 percent coal, and 4 percent wood fuel.

Estimates of fuel consumption in 1985 were based on historical data, although information presented in References 44 through 47 was considered in estimating growth by fuel type and method of firing. Historically the use of fossil fuels in industrial boilers has increased at the rate of about 2 to 4 percent per year. An overall growth rate of 19 percent was used to project 1978 external fuel combustion to 1985. The annual growth rate of ~2.6 percent is less than the Project Independence Evaluation System[44] estimate of 4.5 percent per year and the estimate of 3.7 percent presented in Reference 45, but is about equal to the estimate of 2.6-2.9 percent given in Reference 46 and the projection of 2.3 percent given in Reference 47.

The projection of trends in fuel consumption is subject to large uncertainties and is dependent on future regulatory and national policy decisions and international events that can significantly affect future fuel consumption patterns. At present, firm data regarding the operation of boilers in the

TABLE 70. 1978 AND PROJECTED 1985 INDUSTRIAL FUEL CONSUMPTION

Source category	Fuel consumption (10^{15} joules) 1978	1985	Percent change 1978-1985
Industrial	10,260	11,740	+14
External combustion	8,690	10,320	+19
Coal	1,540	2,002	+30
Bituminous	1,490	1,955	+31
Pulverized, dry	730	876	+20
Pulverized, wet	150	81	-46
Cyclone	40	14	-65
Spreader stokers	510	916	+80
Other stokers	60	68	+13
Anthracite	10	7	-33
All stokers	10	7	-33
Lignite	40	40	0
Spreader stokers	40	40	0
Petroleum	1,710	2,308	+35
Residual oil	1,400	2,028	+45
Tangential firing	170	210	+24
Other	1,230	1,818	+48
Distillate oil	310	280	-10
Tangential firing	50	42	-16
Other	260	238	-8
Gas	4,990	5,470	+10
Tangential firing	500	500	0
Other	4,490	4,970	+11
Other	450	540	+20
Wood/Bark	420	500	+19
Bagasse	30	40	+33
Internal combustion	1,570	1,420	-10
Distillate oil	70	87	+24
Gas	1,500	1,333	-11

Sources: References 1 through 7, and 44 through 47.

industrial sector are limited as is information concerning the future availability of fuels and combustion equipment. The projected increase in the use of coal shown in Table 70 may not materialize because of delays in implementing the national energy plan which calls for reduced reliance on oil and natural gas in favor of coal. Increased use of coal (or wood) by industrial combustion sources also faces certain significant obstacles including the need for fuel storage areas, the imposition of more stringent emission regulations on small boilers, and the cost and availability of combustion and control equipment.

5.2 NATIONWIDE EMISSIONS

The nationwide emissions of criteria pollutants from industrial external combustion sources in 1978 and 1985 were determined based on combined current study and existing data emission factors or EPA emission factors (see Table 58) and the estimated fuel comsumption rates shown in Table 70. Nationwide emission totals for the criteria pollutants are presented in Table 71 and contrasted with emissions from other stationary external combustion source use sectors in Table 72. The industrial sector accounts for about 25, 15, 9, 24, and 28 percent, respectively, of particulate, NO_x, SO_2, CO, and HC emissions from all external combustion sources.

The emissions from the gas- and oil-fired source categories represent uncontrolled emissions. These source categories are generally not subject to control because they do not need controls to meet typical SIP regulations. However, some degree of particulate control for solid fuel-fired boilers is required to meet SIP regulations. Also New Source Performance Standards promulgated in 1974 apply to all new, modified, or reconstructed solid fuel-fired boilers with input capacities greater than 256 GJ/hr, and require approximately 99 percent control of particulate emissions. New Source Performance Standards that would affect industrial boilers are expected to be proposed in the early 1980s. Particulate emission estimates for 1978 were calculated using net control efficiencies of 81 percent for the pulverized units and 53 percent for the spreader stokers and wood stokers. In estimating 1985 emissions it was assumed that the increase in coal use was attributable to new units and a net particulate control efficiency of 90 percent was applied to emissions from these new units. An SO_2 control efficiency of

TABLE 71. 1978 AND PROJECTED 1985 NATIONWIDE EMISSIONS OF CRITERIA POLLUTANTS FROM INDUSTRIAL EXTERNAL COMBUSTION SOURCES

	1978 emissions (Gg/year)					1985 emissions (Gg/year)				
	Particulates	NO_x	SO_2	CO	HC	Particulates	NO_x	SO_2	CO	HC
Natural gas boilers	10	349	1	40	5	11	383	1	44	5
Distillate oil boilers	2	22	33	5	1	2	20	30	4	1
Residual oil boilers	33	187	510	17	3	48	271	740	25	4
Bituminous, pulverized dry bottom boilers	460	256	560	15	4	508	307	582	18	5
Bituminous, pulverized wet bottom boilers	72	88	115	3	1	39	48	62	2	1
Bituminous, spreader stokers	609	148	390	20	10	713	266	702	36	18
Wood stokers	50	21	27	168	42	59	25	33	200	50
Total	1236	1071	1636	268	66	1380	1320	2150	329	85
Percent change 1978-1985						+12	+23	+31	+23	+27

Source: Reference 1 through 7.

80 percent was also applied to SO_2 emissions from the new bituminous, pulverized dry bottom units. Emissions of NO_x were not subjected to control, although it is possible that regulations for NO_x will be promulgated in the future and become effective prior to 1985.

TABLE 72. SUMMARY OF CRITERIA POLLUTANT EMISSIONS FROM STATIONARY EXTERNAL COMBUSTION SOURCES BY USE SECTOR

Use sector	Pollutant emissions (GJ/yr)				
	Particulates	NO_x	SO_2	CO	HC
Electric utilities	3506	5331	16,134	675	83
Industrial	1236	1071	1,636	268	66
Commercial/institutional	262	532	824	89	52
Residential	28	267	269	64	33
Total	5032	7201	19,043	1096	234

Because of the above assumptions regarding the imposition of more stringent control, projected 1985 emissions of particulates are only 12 percent greater than 1978 emissions. The estimated growth in coal consumption was 30 percent over the 1978-1985 period. Gas and oil, which represented 77 percent of the fuel used in 1978, accounted for 4, 52, and 33 percent, respectively, of particulate, NO_x, and SO_2 emissions from industrial external combustion sources. In 1985, it was estimated that gas and oil consumption will drop slightly to 75 percent of the total fuel used by industrial boilers. Projected emissions from gas and oil combustion in 1985 represent 4, 51, and 36 percent, respectively, of total nationwide emissions of particulate, NO_x, and SO_2 from industrial boilers.

Trace element emissions from industrial external combustion sources are summarized in Table 73 for 1978. Emission from gas-fired sources are negligible and are not included in the table. Total emissions were estimated from the fuel consumption data shown in Table 70 and the best available emission factor data. For distillate oil the emission factors used were available values computed from the present study and the existing data base as shown in Table 61. The residual oil emission factors used were those from Reference 21 (see Table 61) because these emission factors represent the weighted nationwide trace element content of residual oils. These values should be more representative of trace element emissions from residual oil-fired boilers than the average of the limited emissions factor data obtained in this study. Emissions from bituminous combustion sources were based on emission factors calculated from data presented in Reference 28, Table 59, adjusted for the particulate control efficiencies and particulate emission factors applicable to the source categories; i.e., bituminous pulverized dry bottom, bituminous pulverized wet bottom, and spreader stoker. Average trace element emission factors measured in this study were used to estimate nationwide emissions from the wood-fired sources.

Trace element emissions from industrial external combustion are predominately the result of coal combustion. Bituminous stokers, rather than pulverized units, are the largest contributor because of the lower level of control applied to stokers in the industrial sector.

Trace element emissions in 1985 can be related to the increase in particulate emissions as previously shown in Table 71. Annual emissions from bituminous pulverized dry bottom boilers in 1985 will be roughly 11 percent greater than 1978 emissions. Trace element emissions from bitiminous pulverized wet bottom boilers will be 46 percent lower in 1985, while emissions from bituminous stokers will shown a 17 percent increase over 1978 emissions. Trace element emissions from the other industrial source categories will be proportional to the changes in fuel consumption shown in Table 70.

POM emissions from industrial sources in 1978 and 1985 are shown in Table 74. The estimates are based on current and projected fuel consumption estimates and POM emission factors measured in this program. The preponderance of POM emissions is from wood combustion. Bituminous stokers are also significant contributors. Total POM emissions in 1985 from industrial sources will amount to about 480 Mg per year, approximately a 25 percent increase over 1978 POM emissions. Industrial POM emissions are approximately 250 percent greater than POM emission estimates given in Reference 28 for electricity generation external combustion sources.

TABLE 73. CURRENT NATIONWIDE EMISSIONS OF TRACE ELEMENTS FROM INDUSTRIAL EXTERNAL COMBUSTION SOURCES

Element	Emissions (Gg/year)					
	Distillate oil-fired boilers	Residual oil-fired boilers	Bituminous, pulverized dry bottom boilers	Bituminous, pulverized wet bottom boilers	Bituminous spreader stokers	Wood boilers
Aluminim (Al)	0.050	0.096	55.2	8.7	71.7	0.11
Arsenic (As)	<0.001	0.020	0.17	0.027	0.22	0.002
Boron (B)	<0.001	0.010	0.57	0.080	0.74	0.024
Barium (Ba)	0.002	0.032	0.58	0.091	0.75	0.018
Beryllium (Be)	<0.001	0.002	0.014	0.002	0.018	<0.001
Bromine (Br)	-	0.003	0.047	0.007	0.061	-
Calcium (Ca)	0.14	0.35	36.6	5.7	47.6	2.8
Cadmium (Cd)	0.002	0.057	0.011	0.002	0.014	<0.001
Cobalt (Co)	<0.001	0.056	4.7	0.74	6.1	<0.001
Chromium (Cr)	0.009	0.033	0.056	0.009	0.73	0.006
Copper (Cu)	0.042	0.070	0.36	0.057	0.46	0.021
Fluorine (F)	-	0.003	1.9	0.30	2.5	-
Iron (Fe)	0.11	0.45	54.6	8.6	71.0	0.17
Mercury (Hg)	-	<0.001	<0.001	<0.001	<0.001	-
Potassium (K)	0.039	0.85	7.4	1.2	9.6	3.7
Lithium (Li)	<0.001	0.002	0.16	0.025	0.21	<0.001
Magnesium (Mg)	0.030	0.33	7.9	1.2	10.3	0.47
Manganese (Mn)	0.013	0.033	0.25	0.039	0.33	0.062
Molybdenum (Mo)	-	0.023	0.070	0.011	0.091	-
Sodium (Na)	0.019	0.78	3.3	0.52	4.3	0.013
Nickel (Ni)	0.068	1.11	0.40	0.063	0.32	0.006
Phosphorus (P)	0.014	0.028	0.58	0.095	0.75	0.24
Lead (Pb)	0.012	0.088	0.13	0.010	0.17	0.009
Antimony (Sb)	<0.001	0.011	0.028	0.004	0.036	<0.001
Selenium (Se)	0.001	0.018	0.042	0.007	0.055	<0.001
Silicon (Si)	0.093	0.44	98.8	15.5	1.28	0.15
Tin (Sn)	-	0.16	0.070	0.011	0.091	-
Strontium (Sr)	0.001	0.004	0.97	0.15	1.3	0.014
Thorium (Th)	<0.001	<0.001	0.008	0.001	0.010	-
Uranium (U)	<0.001	0.018	0.006	0.001	0.008	-
Vanadium (V)	0.024	4.02	0.18	0.028	0.23	<0.001
Zinc (Zn)	0.020	0.002	0.28	0.044	0.36	0.15

TABLE 74. 1978 AND PROJECTED 1985 EMISSIONS OF POM COMPOUNDS FROM INDUSTRIAL COMBUSTION SOURCES

	Emissions (Mg/yr)^a									
	Gas-fired boilers		Residual oil-fired boilers		Bituminous, pulverized wet bottom		Bituminous stokers		Wood-fired boilers	
POM compound	1978	1985	1978	1985	1978	1985	1978	1985	1978	1985
Naphthalene	12.8	14.1	-	-	-		3.4	6.6	114	137
Biphenyl	2.8	3.1	0.3	0.3	0.006	0.005	-		8.0	9.6
Fluorene	-	-	-	-	-		-		0.4	0.3
Phenanthene	0.18	0.20	-	-	0.27	0.22	9.2	18.0	142	170
2-Methyl phenanthene	0.03	0.03	-	-	-		-		24.8	29.8
Fluoranthene	1.8	2.0	-	-	-		3.2	6.3	23.9	28.7
Pyrene	0.14	0.16	-	-	0.033	0.026	8.8	17.2	4.9	5.9
Chrysene	-	-	-	-	-		5.0	9.8	-	
Naphthacene	-	-	-	-	0.12	0.010	-		0.52	0.62
Benzo(g,h,i)fluoranthene	-	-	-	-	-		-		7.6	9.1
Benzo(a)pyrene	-	-	-	-	-		0.7	1.4	9.2	11.0
Benzo(b)fluoranthene	-	-	-	-	-		-		-	
O-phenylene pyrene	-	-	-	-	-		0.005	0.010	-	
Benzo(g,h,i)perylene	-	-	-	-	0.001	<0.001	0.10	0.20	0.7	0.84
Total	17.9	19.6	0.3	0.3	0.43	0.26	30.4	59.5	336	403

^{a}Based on emission factors measured in program.

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APPENDIX A

CRITERIA FOR EVALUATING THE ADEQUACY OF EXISTING EMISSIONS DATA FOR CONVENTIONAL STATIONARY COMBUSTION SYSTEMS

A major task in the present program was to identify gaps and inadequacies in the existing emissions data base for conventional stationary combustion systems. The output from this effort will be used in the planning and performance of a combined field and laboratory program as required to complete adequate emissions assessment for each of the combustion source types.

The criteria for assessing the adequacy of emissions data are developed by considering both the reliability and variability of the data. The general approach is to use a three-step process as described below. This approach is applicable to the evaluation of the existing emissions data as well as emissions data collected during the course of this program.

STEP 1

In the first step of the evaluation process, the emissions data are screened for adequate definition of process and fuel parameters that may affect emissions as well as validity and accuracy of sampling and analysis methods. The screening mechanism is devised to reject emissions data that would be of little or no use. Acceptance of emissions data in this screening step only indicates the possibility for furhter analysis and in no way suggests that these data are valid or reliable. As such, the data screening criteria are often expressed in terms of minimum requiremnets. These screening criteria are depicted in Figure A-1 and discussed in detail below.

The first criterion that will be applied is that only source test data will be accepted. A significant portion of the data base, and especially those contained in the National Emissions Data Systems (NEDS), were developed by the use of standard emission factors* and not derived from actual test data. The inclusion of these estimated emissions data in the data base would lead to the obviously biased conclusion that the actual emissions were the same as those predicted by the standard emission factors.

The second criterion that will be applied is an adequate description of the source. To further analyze the emissions data, there must be sufficient information to designate the combustion source according to the

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*Mostly by the use of emission factors published in the EPA Publication AP-42: Reference A-1.

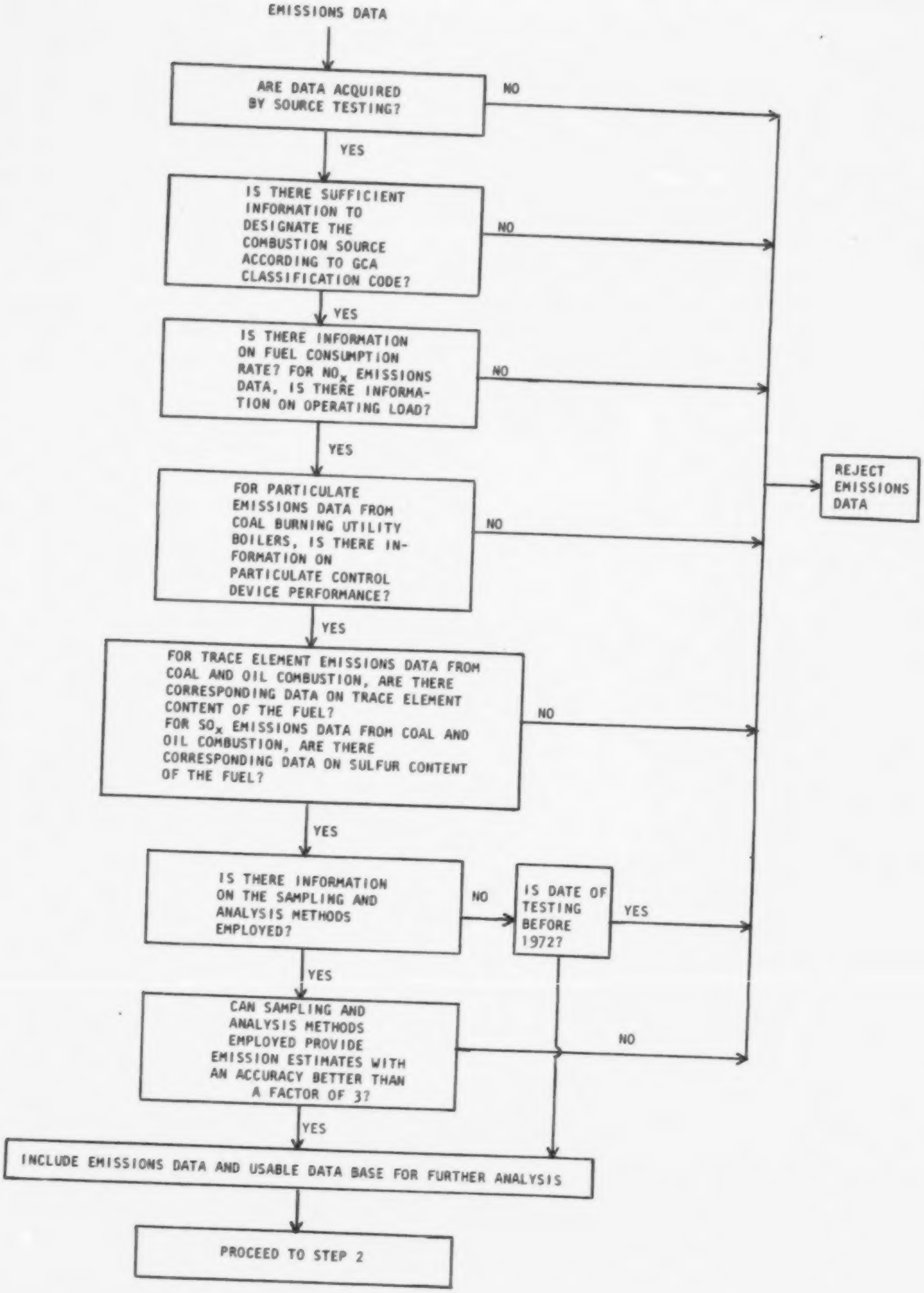
EMISSIONS DATA
ARE DATA ACQUIRED BY SOURCE TESTING?
NO
YES
IS THERE SUFFICIENT INFORMATION TO DESIGNATE THE COMBUSTION SOURCE ACCORDING TO GCA CLASSIFICATION CODE?
NO
YES
IS THERE INFORMATION ON FUEL CONSUMPTION RATE? FOR NO_x EMISSIONS DATA, IS THERE INFORMATION ON OPERATING LOAD?
NO
YES
FOR PARTICULATE EMISSIONS DATA FROM COAL BURNING UTILITY BOILERS, IS THERE INFORMATION ON PARTICULATE CONTROL DEVICE PERFORMANCE?
NO
YES
REJECT EMISSIONS DATA
FOR TRACE ELEMENT EMISSIONS DATA FROM COAL AND OIL COMBUSTION, ARE THERE CORRESPONDING DATA ON TRACE ELEMENT CONTENT OF THE FUEL? FOR SO_x EMISSIONS DATA FROM COAL AND OIL COMBUSTION, ARE THERE CORRESPONDING DATA ON SULFUR CONTENT OF THE FUEL?
NO
YES
IS THERE INFORMATION ON THE SAMPLING AND ANALYSIS METHODS EMPLOYED?
NO
IS DATE OF TESTING BEFORE 1972?
YES
YES
CAN SAMPLING AND ANALYSIS METHODS EMPLOYED PROVIDE EMISSION ESTIMATES WITH AN ACCURACY BETTER THAN A FACTOR OF 3?
NO
YES
INCLUDE EMISSIONS DATA AND USABLE DATA BASE FOR FURTHER ANALYSIS
PROCEED TO STEP 2

Figure A-1. Step 1 Screening Mechanism for Emissions Data appropriate GCA classification code. As a minimum, the information provided should include: the function of the combustion source (electricity generation, industrial, commercial/institutional, or residential), the type of combustion (external combustion or internal combustion), the type of fuel used (coal, oil, gas, or refuse), and in the case of coal combustion, the type of furnace (pulverized dry bottom, pulverized wet bottom, cyclone, or stoker). For emissions data that are judged to be valuable* and otherwise acceptable, efforts will be made to acquire the needed source description information directly from the investigator or the plant operator.

The third criterion for acceptance of emissions data for further analysis is an adequate definition of the combustion system operating mode. For example, operating load has a large effect on NO_x emissions from combustion systems. It is therefore important to have an adequate definition of the test conditions that may affect emissions. As a minimum, there must be information on the fuel consumption rate for the emissions data to be accepted. The fuel consumption rate is necessary for the calculation of emission factors. For NO_x consumption data, field and test results that do not include information on operating load will be considered unacceptable because they cannot be used to estimate emissions from a typical combustion system nor could they be used to estimate emissions at any specific load. For other types of emission data, the operating load information will be considered a useful parameter for data correlation but not an absolute requirement for data acceptance.

The fourth criterion for acceptance of emissions data for further analysis is an adequate definition of the pollution control device performance. Control device performance will affect not only total emissions but will influence, for example, the particle size distribution and composition of flue gas emissions. The application of design efficiencies must be approached with caution in estimating uncontrolled emissions. If a design efficiency of 99 percent is used and if the control device operating efficiency is only 90 percent, the calculated uncontrolled emissions would be 10 times larger than the actual case. Because coal burning utility boilers are equipped with particulate control devices, particulate emissions data from the coal burning utility sector will not be considered acceptable unless accompanied by the particulate control device performance data. The application of particulate control devices is less frequent for the industrial, commercial/institutional and residential sectors, and also much less frequent for the oil burning utility sector and nonexistent for the gas burning utility sector. For these combustion source types, emissions data will be accepted as uncontrolled emissions data, unless there is information implying the contrary. As noted in the foregoing discussions acceptance of emissions data at this screening step does not suggest that the data are necessarily valid or reliable. In the second step of the data evaluation process, methods for rejecting outlying data points will be defined. Controlled emissions data that have been mistakenly assumed to be uncontrolled emissions data because of a lack of information will be identified as outlying data points and be rejected in this second step.

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*In this context, emissions data for trace elements, POM, PCB, and organics are considered to be more valuable because of the paucity of data.

The fifth criterion that will be used to judge the usefulness of the emissions data is the availability of the fuel analysis data. This is especially true for emissions of trace elements and SO_x. The trace element content of coal can vary by one to two orders of magnitude, and emissions are closely related to the trace element content of the coal. No trace elements are present in appreciable amounts in gaseous hydrocarbons; however, nickel, vanadium and sodium are present in appreciable amounts in some fuel oil. To estimate trace element emission levels from all sources within a given category, the fraction of each trace element exiting the system in each effluent stream must be estimated. Thus, trace element emissions data from coal and oil combustion that are not accompanied by analysis data on the trace element content of the fuel will not be accepted. Similarly, SO_x emissions are directly related to the sulfur content of the fuel. SO_x emissions data from coal and oil combustion that do not include information on the sulfur content of the fuel will therefore not be accepted.

The last criterion that will be applied is an evaluation of the accuracy of the sampling and analysis methods used. To determine emissions from a given site to within a factor of 3, both the sampling and analysis procedures used must be capable of providing an accuracy that is better than a factor of 3. The list of methods available for the sampling and analysis of general stream types and chemical classes and species is very extensive and has been described in detail in two recent TRW reports (References A-2 and A-3). In general, most of the sampling and analysis procedures recommended in these two references are adaptations of standard EPA, ASTM, API methods, and have an accuracy and/or precision of ± 10 to 20 percent or better. Emissions data obtained by these recommended methods or techniques will be considered acceptable. Emissions data obtained by methods or techniques not listed in these two references will be subjected to careful review and rejected if it is determined that the sampling or analysis method used would not be able to provide emission estimates within an accuracy factor of 3 or better. Special emphasis will be placed on the review of sampling and analysis methods used for obtaining PCB, POM, particulate sulfate, and trace elements emissions data. In cases where information on the sampling and analysis methods used is unavailable, the date of testing will be used as the criterion for inclusion or rejection of the emissions data in the usable data base. Emissions data obtained before 1972 will be generally considered unacceptable because of probable use of unreliable sampling or analysis procedures. The 1972 cut-off date is selected on the basis that the EPA Method 5 (40-CFR-60, Appendix C, Methods), which has been more or less recognized nationally as the standard method for sampling particulates, was introduced in late 1971. Furthermore, most of the more sophisticated sampling and analysis techniques for obtaining emissions data, and especially those for measuring pollutants for which data are lacking (such as trace elements and particulate sulfate), were not introduced and used before 1972.

STEP 2

In the second step of the data evaluation process, emissions data that have been identified as usable in the screening step will be subjected for further engineering and statistical analysis to determine the internal consistency of the test results and the variability in emissions factors.

Emissions data included in the usable data base will first be categorized according to the 5-column GCA combustion system classification code and the unit operation from which the pollutants are emitted. For NO_x, the emissions data will be further categorized according to the method of NO_x control; no control, staged firing, low excess air, reduced load, or flue gas recirculation. Emissions factors for individual sites, normally expressed in the form of lb/MM Btu or lb/ton, will then be calculated for each pollutant/unit operating pair. In the case of trace element stack emissions from coal and oil combustion, these emission factors will be calculated in the form of the fraction of each trace element emitted to the atmosphere.

The emission factors calculated for each pollutant/unit operation pair will be evaluated in terms of consistency of test results among sites. All the data will be subjected to detailed scrutiny and discarded unless there is additional information to reclassify the data into the correct category. The decision on whether an outlier is a reasonable result or whether it may be discarded as being an improbable member of the group will be based on the method of Dixon. The method of Dixon is a statistical technique applicable to the rejection of a single outlying point from a small group of data and is described in detail in Attachment A.

The variability of the emission factors will next be calculated. The variability is defined as

$$V = \frac{t\ s(\bar{x})}{(\bar{x})} \tag{1}$$

where x is the estimated mean value of the emission factor, $s(\bar{x})$ is the estimated standard deviation of the mean, and t is a multiple of the estimated standard deviation of the mean value $s(\bar{x})$. The value of t depends on the degree of freedom and the confidence level of the interval containing the true mean μ, and is given in standard statistics texts. For the present program, t values at 95 percent confidence level will be used in calculating the variability of emission factors.

The main thrusts in this second step are: (1) to determine the emission factors for each pollutant/unit operation pair and for each combustion source category; (2) to disdard outlying data points using the method of Dixon; and (3) to calculate the percent variability of the emission factors. The values calculated in this step will be used in Step 3.

STEP 3

The final step in the data evaluation process involves a method developed by the Monsanto Research Corporation (MRC) for the evaluation of data adequacy. This quantitative method will indicate where additional emissions data are needed. The method is based on both the potential environmental risks associated with the emission of each pollutant and the quality of the existing emissions data.

The potential environmental risks associated with pollutant emissions are determined by the use of source severity factors S. For emissions to the atmosphere, the souvce severity S is defined as the ratio of the calculated maximum ground-level concentrations of the pollutant species to the level at which a potential environmental hazard exists. The simple Gaussian Plume equation for ground-level receptors at the plume centerline is the dispersion model used for determining the ground-level concentration. The potential environmental hazard level is taken to be the Threshold Limit Value (TLV) divided by 300 for noncriteria pollutants and the ambient air quality standard for the criteria pollutants. The mean source severity S for noncriteria pollutants is calculated as follows:

$$S = \frac{5.5\ Q}{(TLV)h^2} \qquad (2)$$

where Q = emission rate, g/s

TLV = threshold limit value, g/m^3

h = stzck height, m

For the five criteria pollutants, the equations for calculating mean source severity S is given in the following table:

Pollutant	Severity equation	
Particulate	$S = 70Qh^{-2}$	(3)
SO_x	$S = 50Qh^{-2}$	(4)
NO_x	$S = 315Qh^{-2.1}$	(5)
Hydrocarbons	$S = 162.5Qh^{-2}$	(6)
CO	$S = 0.78Qh^{-2}$	(7)

The emission rate is calculated by the following equation:

$$Q = \frac{TC}{TNP}\ (EF)\ (GPP)\ (YPS) \qquad (8)$$

where TC = total fuel consumption, tons/year

TNP = total number of plants/sites

EF = emission factor, lb/ton

GPP = 453.6 g/lb

$YPS = 3.1688 \times 10^{-8}$ yrs

For discharges to the water, the source severity factor S is calculated as follows:

$$S = \frac{V_D\ C_D + f_1 f_2}{V_R D} \qquad (9)$$

where V_D = discharge flow rate, m^3/s

C_D = discharge concentration, g/m^3

S_G = leachable solid waste generation, g/sec

f_1 = fraction of the solid waste to water

f_2 = fraction of the material in the solid waste

V_R = river flow rate, m^3/s

D = drinking water standard, g/m^3

The mean source severity factor S for each pollutant/unit operation pair will be used in the evaluation of data adequacy. The method for evaluating data adequacy is outlined below.

Case 1: When Emissions Data Are Available and Usable

1. Determine the mean emission factor $\bar{x}$ and the variability of the emission factor $ts(\bar{x})/\bar{x}$ for each pollutant/unit operation pair. (This will be done in Step 2 of the data evaluation process.)

2. Determine the mean severity factor S for each pollutant/unit operation pair by using the mean emission factor $\bar{x}$.

3. If the variability in emission factor < 70 percent, additional data are not needed.

4. If the variability in emission factor > 70 percent and $S > 0.05$, the current data base is judged to be inadequate and there is need for additional data.

5. If the variability in emission factor > 70 percent and $S \leq 0.05$, determine the severity factor S_u by using the emission factor $\bar{x}_u$:

$$\bar{x}_u = \bar{x} + ts(x)$$

S_u is the upper bound for the severity factor S. The current data base is judged to be adequate if $S_u \leq 0.05$ and inadequate if $S_u > 0.05$.

Case 2: When Emissions Data Are Not Available

1. Determine, if possible, from fuel analysis, mass balance and physico-chemical considerations the upper bound $\bar{x}_u$ of the emission factor x. For trace element stack emissions, for example, $\bar{x}_u$ can be determined by assuming that all the trace elements present in the fuel are emitted through the stack.

2. Determine the upper bound S_u of the severity factor S for each pollutant/unit operation pair by using the emission factor $\bar{x}_u$.

3. The current data base is judged to be adequate if $S_u \leq 0.05$ and inadequate if $S_u > 0.05$.

As discussed in a recent Monsanto report (Reference A-4), an allowable uncertainty in emission factor of ± 70 percent (factor of 3) would lead to an uncertainty of less than 10 in S_{calc}, which has been defined as the acceptable uncertainty factor for S.

As a result of the application of the above data evaluation criteria, pollutant/unit operation pairs that have been inadequately characterized will be identified to permit the planning of field tests for acquisition of additional emissions data.

ATTACHMENT A

METHOD OF DIXON FOR DISCARDING OUTLYING DATA*

The method of Dixon provides a test for extreme values using range. If the observations in the sample are ranked, the individual values can be identified $x_1, x_2, x_3, \ldots, x_{n-1}, x_n$. It is immaterial whether the ranking proceeds from high values to low or from low values to high. The Dixon extreme-value test gives the maximum ratio of differences between extreme-ranking observations to be expected at various probability levels and for different sample sizes. Table A-1 gives the test ratios and maximum expected values. For samples less than about eight observations, the ratio of the difference between the extreme and the next-to-extreme value to the total range is compared with the tabulated values for the same sample size. If the observed ratio exceeds the tabulated maximum expected ratio, the extreme value may be rejected with the risk of error set by the probability level. For samples between about 9 and 14, the ratio of the difference between the first and third ranking observations to the difference between the first and next to last is tested. For samples of 15 or more, the ratio of the difference between the first and the third ranking observations to the difference between the first- and the second-from last observation is used.

In the evaluation of the emissions data, the 0.05 probability level will be used as the basis for discarding outlying data.

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*Volk, W. Applied Statistics for Engineers. New York McGraw-Hill, Inc. 2nd ed. p. 387-388. 1969.

TABLE A-1. MAXIMUM RATIO OF EXTREME RANKING OBSERVATIONS

			Maximum ratio		
			Probability level		
Recommended for sample size	Rank difference ratio	Sample size, n	0.10	0.05	0.01
$n < 8$	$\frac{x_2 - x_1}{x_n - x_1}$	3	0.886	0.941	0.988
		4	0.679	0.765	0.889
		5	0.557	0.642	0.780
		6	0.482	0.560	0.698
		7	0.434	0.507	0.637
$8 < n < 15$	$\frac{x_3 - x_1}{x_{n-1} - x_1}$	8	0.650	0.710	0.829
		9	0.594	0.657	0.776
		10	0.551	0.612	0.726
		11	0.517	0.576	0.679
		12	0.490	0.546	0.642
		13	0.467	0.521	0.615
		14	0.448	0.501	0.593
$n > 15$	$\frac{x_3 - x_1}{x_{n-2} - x_1}$	15	0.472	0.525	0.616
		16	0.454	0.507	0.595
		17	0.438	0.490	0.577
		18	0.424	0.475	0.561
		19	0.412	0.462	0.547
		20	0.401	0.450	0.535

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A-4. Eimutis, E. C. Source Assessment: Prioritization of Stationary Air Pollution Sources--Model Description. Report prepared by Monsanto Research Corporation for the U.S. Environmental Protection Agency. EPA-600/2-76-032a. February 1976.

APPENDIX B

DATA REDUCTION PROCEDURE

Stack emissions data reported from field measurements or laboratory analyses are often expressed in terms of volume concentration (ppmv) or mass concentration (mg/m³, μg/m³). To convert these emissions data to the emission factor form, the following data reduction procedure, adopted from Reference B-1, is used.

The number of gm moles of flue gas per gm of fuel can be computed using the fuel composition analysis and effluent O_2 concentration:

$$n_{FG} = \frac{4.762\ (n_C + n_S) + 0.9405\ n_H - 1.881\ n_O}{1\text{-}4.762\ (O_2/100)} = \frac{F}{1\text{-}4.762\ (O_2/100)}$$

where: n_{FG} = gm moles of dry effluent/gm of fuel under actual operating conditions

n_j = gm moles of element j in fuel per gm of fuel

O_2 = volumetric O_2 concentration in percent

F = gm moles of dry effluent/gm of fuel under stoichiometric combustion

The average values of F for natural gas and various liquid fuels are given in Table B-1. The value of F for coal must be computed on an individual basis because of the variation in the elemental composition of different coals.

For emission species measured on a volumetric concentration basis (ppmv), the emission factor expressed as ng/J can be computed using the following equation:

$$\left\{\begin{matrix}\text{Emission}\\ \text{Factor}\end{matrix}\right\}\ (\text{ng/J}) = \frac{\left\{\begin{matrix}\text{Volumetric}\\ \text{Concentration}\end{matrix}\right\}_s\ (\text{ppmv}) \times F \times M_s}{\left\{\begin{matrix}\text{Fuel}\\ \text{Heating Value}\end{matrix}\right\}\ (\text{kJ/kg fuel})} \times \frac{1000}{1\text{-}4.762\ (O_2/100)}$$

where s = subject emission species

M_s = molecular weight of species s

TABLE B-1. ELEMENTAL COMPOSITION AND HIGHER HEATING VALUE OF FUELS*

Fuel	Natural gas	No. 2 distillate oil	Kerosene	Residual oil
n_C	0.06221	0.06994	0.06994	0.07160
n_S	0	0.00006	0	0.00031
n_H	0.23116	0.13889	0.15873	0.10913
n_O	0.00040	0.001125	0	0.00125
F	0.51215	0.45983	0.48234	0.44037
Heating Value	53,310 kJ/kg	45,040 kJ/kg	47,710 kJ/kg	43,760 kJ/kg

*The composition and heating value data are obtained from Reference B-2.

For emission species measured on a mass concentration basis (mg/m^3 or µg/m^3) at 20°C, the emission factor expressed as ng/J, can be computed using the following equation:

$$\begin{Bmatrix}\text{Emission}\\ \text{Factor}\end{Bmatrix} (\text{ng/J}) = \frac{\begin{Bmatrix}\text{Mass}\\ \text{Concentration}\end{Bmatrix}_s (\mu\text{g/m}^3) \times F \times 24.04}{\begin{Bmatrix}\text{Fuel}\\ \text{Heating Value}\end{Bmatrix} (\text{kJ/kg fuel})} \times \frac{1}{1-4.762\ (O_2/100)}$$

The higher heating values of natural gas and various liquid fuels are also given in Table B-1.

Note that the data reduction procedure described here significantly minimizes errors introduced in data reduction by eliminating terms that are subject to large measurement errors, such as stack velocity and temperature measurements. The only stack parameter needed in data reduction is the volumetric O_2 concentration, which can usually be determined by gas chromatography with great accuracy.

Example Calculation--

The NO_x emission from a gas fueled gas turbine is reported to be 200 ppmv at an O_2 effluent concentration of 15 percent. Calculate the emission factor for NO_x (as NO_2) in ng/J.

Emission factor for NO_x (as NO_2)

$$= \frac{200 \times 0.51215 \times 46.0}{53310} \times \frac{1000}{1-4.762 \times 0.15}\ \text{ng/J}$$

$$= 309\ \text{ng/J}$$

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APPENDIX C

SUMMARY OF EXISTING EMISSIONS DATA

TABLE C-1. EMISSION RATES OF CO, HYDROCARBONS, PARTICULATES, NO$_x$, AND SO$_2$ FROM NATURAL GAS-FIRED INDUSTRIAL BOILERS

Site no.	Reference no.	Emissions (ng/J)					Burner Type[a]	Boiler type[b]	Firing rate (GJ/hr)	Capacity factor (percent)	Boiler efficiency (percent)	System age (year)	Stack gas			Excess air (percent)	Bacharach smoke no.
		CO	Hydrocarbons	Particulates	NOx (as NO_2)	SOx (as SO_2)							Percent O_2	Percent CO_2	Temp. (°C)		
1	1	54	5.5	2.7	38		R	WT	26.4	80	78	1954	2.9	9.6	254		
2	1	52			37		R	WT	30.6	76	80	1964	3.4	9.6	238		
3	1	46	7.6	1.1	51	3.3	R	WT	30.6	83	77	1964	2.9	10.0	238		
4	1	327	5		60.5		R	WT	63.3	81	77	1950	3.0	9.9	311		
5	1	0		1.9	54.3		R	WT	63.3	80	80	1960	5.2	9.3	238		
6	1	3.1		2	126		R	WT	63.3	77	79	1948	2.6	10.6	182		
7	1	17		2.8	195		R	WT	168.8	85	76	1968	3.8	9.8	310		
8	1	0	6.2	0.5	150		R	WT	168.8	79	79	1971	12.0	4.6	135		
9	1	0	0.5	3.6	104		R	WT	316.5	86	84	1971	3.1	10.4	145		
10	1	0	2.4	2.7	29		R	FT	10.6	80		1968	5.1	8.4	135		
11	1	0	11	8.3*	56		R	FT	21.1	70	80	1960	6.8	7.6	204		
12	1	50			48		R	FT	11.6	95	83	1970	3.6	10.1	177		
13	1	65	10.3		39		R	FT	7.4	87		1969	5.0	8.6			0.0
14	1	55	50.2		48		R	FT	10.6	70	82	1968	8.0	7.4			
15	1	0	4.5		31		R	FT	13.7	95		1959	4.1	9.6			0.0
16	1	4.3	4.8		31		R	FT	19.0	96	82	1971	7.2	7.7	149		0.0
17	1	45	103*		43		R	FT	21.1	63	83	1968	2.8	10.0	177		
18	1	0	6	1.9	37		R	FT	8.4	80			11.0	4.8	104		
19	1	0		2.4	47	3.1	R	WT	34.8	73	78	1970	4.5	9.2	152		
20	1	31			51		R	WT	69.6	82		1963	3.8	9.4			
21	1		1.4	2.5	111		N	WT	237.2	80	84	1966	6.0	9.0	171		
22	1	0	1	4.6	167		N	WT	342.7	81	85	1968	4.5	9.3	177		
23	1	0		2.5	49		R	WT	116.1	77	70	1963	8.1	7.8	271		
24	2	152			38		R	WT	30.6	83	81	1964	0.9	11.2	293		
25	2	0			56.6		R	WT	106	75	82	1967	6.6	7.9	171		
26	2	0	22		78.5		R	WT	158.2	80	82	1972	5.3	8.0	143		
27	2	0			117		R	WT	180	69	83	1963	4.4	9.4	160		
28	2	100	6.9		96.4		N	WT	264	78		1972	2.6	11.4	377		
29	2	0	1.8		112		R	WT	47.5	89	82	1951	1.9	9.4	227		
30	2	3.1	1.0		30		R	WT	18.5	80	80	1970	3.2	10.0	254		
31	7	1.2	0.7		74.4	0	R	WT	15.3•	83	78	1970	3.0	10.2	281		
31	7	5.9	0.9		70.4	0	N	WT	14.6•	79	78	1970	3.2	11.0	264		
31	7	7.1	0.2	3.68	64.9			WT	20.9	82	78	1970	3.3	10.5	268		
32	7	43.3					R	WT	42.3•	89	81		1.6	10.5	223		

[a] Burner Type: R -- Ring
N -- Nozzle

[b] Boiler Type: WT -- Water Tube
FT -- Fire Tube

*Discarded as outlying point by Dixon Method (see Appendix C, Attachment A).

•Boiler steam load reported in lieu of firing rate.

TABLE C-2. EMISSION RATES OF CO, HYDROCARBONS, PARTICULATES, NO_x, AND SO_2 FROM DISTILLATE OIL-FIRED INDUSTRIAL BOILERS

Site no.	Reference no.	Emissions (ng/J)					Firing Method[a]	Boiler type[b]	Firing rate (GJ/hr)	Capacity factor (percent)	Boiler efficiency (percent)	System age (year)	Fuel characteristics		Stack gas			Excess air (percent)	Bacharach smoke no.
		CO	Hydrocarbons	Particulates	NOx (as NO_2)	SOx (as SO_2)							Percent S	Fuel oil no.	Percent O_2	Percent CO_2	Temp. (°C)		
1	1	0		8.4	98	84	S	WT	116.0	80	87	1967	0.18	2	5.7	11.6	279		
2	1		18.6^{+}	17.6	93	68	A	FT	10.6	70	84	1968	0.23	2	7.2	9.5	145		
3	1	16.5		16	36	48	S	WT	18.5	80	85	1970	0.06	2	3.6	12.6	246		
3	1	0	0.5		54		A	WT	18.5	80	85	1970	0.06	2	3.0	13.1	224		
3	1	0	0	8.3	44		M	WT	18.5	69	85	1970	0.06	2	4.3	12.0	260		
4	1	0			71		A	FT	11.6	103	88	1970	0.48	2	4.7	11.8	113		
5	1	0			64		A	FT	19.0	88	85	1971	0.48	2	8.0	9.4	154		0.0
5	1	0			65		S	FT	19.0	87	86	1971	0.48	2	8.0	9.6	154		1.5
6	1	0	5.3	12.1	106	116	A	FT	21.1	80	85	1960	0.30	2	5.8	10.2	202		
7	2	139^{+}		7.7	47.7	300^{+}	S	WT	30.6	86	83	1964	0.40	2	2.7	13.2	243		
8	1	0			70		A	FT	7.4	96		1969	0.38	2	6.8	10.5			1.0
9	1	0	1.9	12.5	100	72	S	WT	169.0	73	84	1971	0.23	2	5.2	7.7	124		
10	1	0		16.8	68	85	S	WT	34.8	70	81	1970	0.22	2	5.9	10.8	141		
11	1	0			46		A	FT	13.7	85		1959	0.19	2	3.1	12.7			
12	7	1.4	0.4	24.24	67.4	71.5		WT	18.8	83	82	1970	0.16	2	3.2	13.5	269		
13	7	4.1	1.2		64.6	95.8		WT	19.0	80	83	1970	0.16	2	2.9	13.2	266		
14	8	3			49		A		2.6*	67			0.24	2				17	0.5
14	8						A		3.7*	95			0.24	2				17	
14	8	6			51		A		2.1*	54			0.24	2				17	0.0
14	8	3			64		A		2.6*	68			0.24	2				35	1.5
14	8						A		3.7	95			0.24	2				35	

[a] Firing Method:
S -- Steam Atomized
A -- Air Atomized
M -- Mechanical Atomization

[b] Boiler Type:
WT -- Water Tube
FT -- Fire Tube

$^{+}$Boiler steam load reported in lieu of firing rate.

*Discarded as outlying point by Dixon Method (see Appendix C, Attachment A).

TABLE C-3. EMISSION RATES OF CO, HYDROCAPBONS, PARTICULATES, NO_x, AND SO_2 FROM RESIDUAL OIL-FIRED INDUSTRIAL BOILERS

Site no.	Reference no.	Emissions (ng/J)					Firing Method[a]	Boiler type[b]	Firing rate (GJ/hr)	Capacity factor (percent)	Boiler efficiency (percent)	System age (year)	Fuel characteristics		Stack gas			Excess air (percent)	Bacharach smoke no.
		CO	Hydrocarbons	Particulates	NOx (as NO_2)	SOx (as SO_2)							Percent S	Fuel oil no.	Percent O_2	Percent CO_2	Temp. (°C)		
1	1	0	6.2		193	1109	S	WT	18.5	80	85	1970	2.8	6	3.6	13.4			
1	1	0			184	1056	A	WT	18.5	86	85	1970	2.8	6	4.4	12.9			
2	1	0		48	110	664	C	WT	20.3	63	74	1948	1.59	5	7.6	10.4	318		
3	1	28.4	24.6[+]		181		S	WT	90.0	69	86	1950	0.35	5	7.6	10.2	143		
4	1	0		37	168	368	S	WT	84.4	64	80	1966	1.53	6	5.7	11.4	296		
5	1	0		47	136	370	S	WT	95.0	79	82	1935	1.04	6	7.4	10.7	371		
6	1	0		49	103	373	S	WT	68.6	83	85	1962	1.03	6	4.7	12.4	216		
7	1	0		28	138	387	S	WT	111.0	76	83	1946	1.03	6	6.3	11.2	224		
8	1	0		20	132	416	S	WT	168.8	81	86	1965	1.03	6	6.8	11.0	207		
9	1		1.2	161	147	1151	S	WT	527.0	80	78	1967	2.43	6	9.5	9.2	224		
10	1	7.2	1.4	210	164	864	A	FT	7.4	96	88	1969	1.85	6	5.4	11.8			2.3
10	1	0			152		A	FT	7.4	96		1969	2.4	5	6.3	11.2			2.0
11	1	0		27	101	630	A	FT	11.6	108	87	1970	1.46	5	4.1	12.8	166		
12	1	0		28	98	601	A	FT	19.0	98	86	1971	1.46	5	7.3	10.4	160		1.0
12	1	4.3		34	89	619	S	FT	19.0	96	86	1971	1.46	5	6.7	10.9	160		
13	1	0	1	37	100	611	A	FT	13.7	84	85	1959	1.3	5	3.2	13.2			0.0
14	1	12	13.4	17	341	426	S	WT	10.6	78	82	1950	0.63	5	2.9	13.0	304		
15	1				257	371	S	WT	69.6	77	78	1963	0.63	5	5.8	10.8	299		
16	1			18.5	185	362	S	WT	131.9	80	77	1972	1.15	5	6.4	10.4	316		
17	2	40[+]		30.9	257	488	S	WT	106.0	85	81	1967	1.29	5	9.3	8.8	168		
18	2	0	6.8		165		S	WT	158.0	73	87	1972	2.74	6	5.0	11.8	154		
19	2	0	1.6		148		S	WT	121.0	78	82	1966	1.60	6	3.3	13.5	332		3.0
20	2	0	2.9	61.9	109	815	S	WT	42.0	80	85	1955	1.91	6	4.3	12.6	218		5.0
21	2	0		45.6	183	738	S	WT	47.5	80	87	1951	0.19	6	3.0	11.0	204		
22	2	0		13.3	95		S	WT	18.5	80	84	1970	0.37	6	3.1	13.2	254		1.5
22	2	0	0	13.3	91	146	A	WT	18.5	80	83	1970	0.37	6	2.9	13.2	254		1.0
23	7	7	0.2	6.26	118	305		WT	21.8	82	82	1970	0.55	6	2.9	13.9	267		
23	7	12	1.3	39.5	135	638		WT	20.6	83	82	1970	1.17	6	3.0	13.8	269		
23	7	1.4	2.1	36.71	120.3	254.7		WT	19.9	79	83	1970	0.54	6	3.0	13.6	266		
23	7	1.4	1.2		123.1	277.2		WT	20.0	80	83	1970	0.54	6	3.1	13.6	269		
24	7	7.5		66.4		759.2		WT	70.1	84	85		1.88	6	2.9	13.8	228		
25	8	10			153		A		3.6*	92				6				17	4
25	8	8			132		A		3.0*	76				6				17	7
25	8	9			162		A		3.6*	92				6				35	2
25	8	7			160		A		3.0*	76				6				35	3

[a] Firing Method:
S -- Steam Atomization
A -- Air Atomization
C -- Cup Burner

[b] Boiler Type:
WT -- Water Tube
FT -- Fire Tube

[+] Discarded as outlying point by Dixon method (see Appendix C, Attachment A).

[*] Boiler steam rate reported in lieu of firing rate.

TABLE C-4. EMISSION RATES OF CO, HYDROCARBONS, PARTICULATES, NO_x, AND SO_2 FROM BITUMINOUS COAL-FIRED INDUSTRIAL BOILERS

Site no.	Reference no.	Emissions (ng/J)					Firing Method[a]	Boiler type[b]	Firing rate (GJ/hr)	Capacity factor (percent)	Boiler efficiency (percent)	System age (year)	Fuel characteristics		Stack gas		
		CO	Hydrocarbons	Particulates	NOx (as NO_2)	SOx (as SO_2)							Percent S	Percent ash	Percent O_2	Percent CO_2	Temp. (°C)
1	1	0			160	449	UFS	WT	63.5	80	76	1941	0.86	9.51	6.6	12.7	243
2	1	0		570	135		UFS	WT	63.5	77	72	1943	0.86	9.51	9.8	10.4	260
3	1	13	6	1,235	223	1,544	SS	WT	142	81	82	1958	2.94	4.77	7.0	12.0	232
4	1	13	3	360	280	1,563	SS	WT	53	80	81	1947	0.76	6.75	8.0	10.6	260
5	1	46	3	103	280	1,420	SS	WT	79	84	76	1957	1.55	6.94	7.8	10.7	332
6	1	0	4	446	228	1,555	P	WT	237	80	86	1966	4.20	9.36	5.3	13.6	188
7	1	0		996	464	1,123	SS	WT	222	80	81	1950	1.58	7.99	10.2	9.8	166
8	1			205	329	782	SS	WT	292	70	80	1969	0.86	10.36	10.8	9.6	185
9	1		1,434	4,419	349	1,340	P	WT	527	80	81	1967	1.68	17.37	9.8	10.0	224
10	1	0		527	482	949	C	WT	540	80	88	1967	2.92	7.78	3.4	15.0	145
11	1	121		263	164		UFS	FT	10.5	80	--	1948	1.50	4.58	4.9	4.8	199
12	1	402		530	208		UFS	FT	10.5	80	--	1948	1.50	4.58	18.0	2.0	143
13	1	0	2	705	291	1,524	P	WT	343	81	86	1971	2.74	11.58	5.8	13.2	179
14	2	0		1,320	196	947	SS	WT	177	66	87	1963	1.16	9.71	6.2	12.8	160
15	2	0		1,140	216		P	WT	527	83	76	1967	1.36	14.48	8.6	8.6	216
16	3	15.3			155.8		OFS	WT	55.7	75	77	1966	2.8	8.03	6.6	10.9	
16	3	37.9		808	128.9	1,867	OFS	WT	60.8	82	78	1966	2.8	8.03	6.6	11.4	
17	3	56.7					SS	WT	63.3*	60	--	1952	0.73	8.29	7.9	11.0	
17	3	207		888		919	SS	WT	95.*	90	74	1952	0.73	8.29	7.2	12.1	254
17	1	17.7		674		1,711	SS	WT	63.3*	60	77	1952	3.07	9.6	10.0	10.3	193
17	3	121		644		1,924	SS	WT	95.*	90	76	1952	3.07	9.6	9.1	10.3	216
18	3	117			273	2,025	SS	WT	113.1*	67	81	1960	2.28	7.76	8.6	9.2	
18	3	137			288	1,838	SS	WT	118.2*	70		1960	2.28	7.76	8.2	9.7	
18	3	54			300		SS	WT	121.5*	72		1960	2.28	7.76	8.2	9.9	211
18	3	137			314	1,777	SS	WT	118.2*	70		1960	2.28	7.76	8.4	9.7	
18	3	108			254	2,043	SS	WT	131.7*	78		1960	2.28	7.76	6.6	11.1	
18	3	189			241	1,755	SS	WT	131.7*	78	83	1960	2.28	7.76	6.5	11.2	211
18	3	201			222	826	SS	WT	113.1*	67		1960	1.15	9.12	7.8	10.3	
18	3	327			236	703	SS	WT	118.2*	70		1960	1.15	9.12	7.3	10.4	
18	3	196		10,956	238	674	SS	WT	103*	61	77	1960	1.15	9.12	7.9	10.1	206
18	3	298			243	660	SS	WT	108*	64		1960	1.15	9.12	7.6	10.4	
18	3	239			224	898	SS	WT	133.4*	79		1960	1.15	9.12	6.7	11.4	
18	3	818		12,234$^+$	192	819	SS	WT	135*	80		1960	1.15	9.12	6.0	11.9	177
18	3	373			229		SS	WT	121.5*	72	79	1960	1.15	9.12	6.9		
19	3	19			203	1,422	SS	WT	51.5*	61		1951			9.1	8.9	
19	3	14		618	196		SS	WT	51.5*	61	78	1951			9.3	8.5	255
19	3	15			239		SS	WT	60.8*	72		1951			8.0	9.2	
19	3	19		757	191	1,657	SS	WT	62.5*	74	80	1951	2.04	8.69	8.0	9.5	251
19	3	29			170	1,308	SS	WT	63.3*	75		1951			7.0	10.9	
19	3	27		1,104	185	1,391	SS	WT	64.1*	76	78	1951	1.74	8.96	7.0	11.0	273
19	3	111			207	1,554	SS	WT	59.9*	71		1951			8.3	10.7	

(continued)

TABLE C-4. EMISSION RATES OF CO, HYDROCARBONS, PARTICULATES, NO_x, AND SO_2 FROM BITUMINOUS COAL-FIRED INDUSTRIAL BOILERS (continued)

Site no.	Reference no.	Emissions (ng/J)					Firing method[a]	Boiler type[b]	Firing rate (GJ/hr)	Capacity factor (percent)	Boiler efficiency (percent)	System age (year)	Fuel characteristics		Stack gas		
		CO	Hydrocarbons	Particulates	NOx (as NO_2)	SOx (as SO_2)							Percent S	Percent ash	Percent O_2	Percent CO_2	Temp. (°C)
20	3	58		617		366	SS	WT	9.0*	63		1958	0.58	5.29	14.2	5.7	
21	3		17.8+			772	P	WT	123.2*	73	88	1956	1.16	7.76	3.6	14.9	160
21	3		8.1	1,176	147	208	P	WT	121.5*	72	88	1956	0.32	8.91	3.8	14.4	153
22	3			2,147	227	2,582	P	WT	211.1*	87	87	1950	3.71	16.99	3.1	14.7	
23	3				134	2,105	VS	WT	42.3*	89		1964	2.81	7.25	5.5		
23	3	253			113	1,976	VS	WT	46.5*	98		1964	2.81	7.25	4.7	14.0	
23	3	11		276	107		VS	WT	31.8*	67		1964	2.81	7.25	8.2	11.0	
23	3				101	412	VS	WT	34.7*	73		1964	0.83	3.92	4.5	14.2	
23	3	35			107	708	VS	WT	37.5*	79		1964	0.83	3.92	7.5	11.9	
23	3	818		97	89	581	VS	WT	31.8*	67		1964	0.83	3.92	7.8	11.1	
23	3	818			95	515	VS	WT	31.8*	67		1964	0.83	3.92	7.8	10.6	
23	3	818			86	603	VS	WT	31.3*	66		1964	0.83	3.92	6.3	11.5	
24	4	154		4,214	178		S		328	70	81	1976	0.75	3.27	5.1		
25	5	13		417	92	1,033	VS	*	85	79	84	1964	1.23	5.86	8.1	11.2	
26	6	0	0.869	4,174		651	P	-	132[c]		84		0.91	8.23			

[a] Firing Methods:
UFS -- Under Feed Stoker
SS -- Spreader Stoker
P -- Pulverized Coal (dry bottom)
C -- Cyclone
CH -- Chain Grate Stoker
OFS -- Over Feed Stoker
VS -- Vibrating Stoker
S -- Stoker

[b] Boiler Types:
WT -- Water Tube
FT -- Fire Tube

[c] System capacity reported in lieu of firing rate.

*Boiler steam load reported in lieu of firing rate.

+Discarded as an outlying point by Dixon method. (see Appendix C, Attachment A).

C-5

R

TABLE C-5. EMISSION RATES OF HYDROCARBONS, PARTICULATES, NO_x AND SO_2 FROM UNCONTROLLED AND MULTICLONE CONTROLLED WOOD/BARK-FIRED BOILERS

Site No.	Reference No.	Emissions (ng/J)				Firing method[a]	Particulate control technique[b]	Reinjection[c]	Firing rate GJ/hr	Capacity factor (percent)	Fuel characteristics		
		Hydrocarbons	Particulates	NO_x (as NO_2)	SO_2						Percent moisture	Percent ash	Percent S
33	9		141.			DO	N		11.[d]	73	40		
34	9		61.4			SD	N		39.[d]	82	4		
35	9		87.9			DO	N		35.[d]	95			
36	9		82.7			DO	N		13.[d]	109			
37	9		92.9			SS	MC		11.[d]	67			
38	9		795.			DO	N		2.4[d]	112			
39	9		114.			DO	MC		16.[d]	63	43		
40	9		122.			DO	MC	R	21.[d]	80	45		
41	9		112.			DO	MC	RS	25.[d]	72	46		
42	9		220.			DO	N		4.1[d]	75	46		
42	9		694.			DO	N		3.7[d]	67			
43	9		201.			DO	MC		5.5[d]	100			
44	9		191.			DO	N		3.3[d]	80			
45	9		140.			DO	MC		19.[d]	62	38		
46	9		157.			DO	MC	R	21.[d]	80	45		
47	9		166.			SS	MC		20.[d]	75	35-40		
48	9		137.			DO	MC		54.[d]	79	41		
48	9		410.			DO	N		46.[d]	68			
49	9		561.			DO	N		5.5[d]	100			
50	9		136.			DO	N		12.[d]	78	40		
51	9		184.			DO	MC		75.[d]	78	45		
51	9		432.			DO	MC		64.[d]	67	50		
52	9		502.			DO	N		5.5[d]	100			
53	9		184.			SS	N		54.[d]	102			
54	9		214.			DO	MC	RS	50.[d]	89	42		
54	9		411.			DO	MC	RS	39.[d]	70	33		
55	9		238.			DO	N		22.[d]	82			
56	9		258.			DO	N		7.2[d]	85			
57	9		269.			DO	N		17.[d]	93	30-50		
58	9		550.			DO	N		24.[d]	75	45		
59	9		135.			SD	MC		35.[d]	67			
60	9		201.			DO	MC		51.[d]	90			
61	9		127.			DO	N		53.[d]	77			
62	9		197.			DO	N		42.[d]	80	40		
63	9		188.			SS	MC	R	84.[d]	93	40		
64	9		279.			DO	N		42.[d]	80			

(continued)

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TABLE C-5. EMISSION RATES OF HYDROCARBONS, PARTICULATES, NO_x AND SO_2 FROM UNCONTROLLED AND MULTICLONE CONTROLLED WOOD/BARK-FIRED BOILERS
(continued)

Site No.	Reference No.	Emissions (ng/J)				Firing method[a]	Particulate control technique[b]	Reinjection[c]	Firing rate GJ/hr	Capacity factor (percent)	Fuel characteristics		
		Hydrocarbons	Particulates	NO_x (as NO_2)	SO_2						Percent moisture	Percent ash	Percent S
65	9		152.			DO	MC	R	23.[d]	85			
66	9		213.			DO	MC	R	11.[d]	76	47		
66	13	18.0				DO	MC	R	11.[d]	76			
67	9		185.			DO	N		6.8[d]	65	45		
68	9		252.			DO	MC	R	88.[d]	100	65		
69	9		17.8			SS	MC		79.[d]	68			
70	9		291.			DO	MC	R	27.[d]	87	30		
71	9		640.			DO	N	R	24.[d]	75	45		
72	9		239.			DO	MC		71.[d]	104	41		
73	9		465.			DO	N		3.6[d]	112			
74	9		285.			SS	MC		74.[d]	70			
75	9		338.			DO	MC		24.[d]	79	51		
76	9		1130.			DO	N		5.0[d]	100	42		
77	9		419.			SS	MC		110.[d]	86	43		
78	9		865.			DO	N		33.[d]	100			
79	9		366.			SS	MC	R	45.[d]	85			
80	9		362.			SS	MC	RS	84.[d]	80	50		
81	9		380.			SS	MC	R	45.[d]	71			
81	13	50.7				SS	MC	R	58.[d]	92			
82	9		611.			DO	N		24.[d]	75	45		
83	9		619.			DO	N		24.[d]	75	45		
84	9		343.			SS	MC	R	76.[d]	104	50		
84	9		521.			SS	MC	R	84.[d]	114	50		
85	9		443.			SS	MC		150.[d]	82			
86	9		561.			SS	MC	RS	210.[d]	98			
87	9		525.			SS	MC	RS	66.[d]	60			
87	9		787.			SS	MC	RS	81.[d]	74			
88	9		510.			SS	MC		29.[d]	68	41		
89	9		766.			SS	MC		44.[d]	83			
90	9		657.			SS	MC	RS	150.[d]	64			
91	9		767.			SS	MC	RS	100.[d]	66			
92	10		111.	<6.		DO	N		5.8		23	0.85	0.025
93	10		308.			DO	N		6.4		11	0.32	0.019
94	10		57.6			DO	N		5.9		8.3	1.12	0.007
95	10			6.		PS	C		8.7		5.9	0.33	0.004
96	10		445.	5.		PS	N		7.4		5.3	0.44	0.018
97	10		150.	5.		DO	N		9.9		11	8.0	0.057

(continued)

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TABLE C-5. EMISSION RATES OF HYDROCARBONS, PARTICULATES, NO_x AND SO_2 FROM UNCONTROLLED AND MULTICLONE CONTROLLED WOOD/BARK-FIRED BOILERS (continued)

Site No.	Reference No.	Emissions (ng/J)				Firing method[a]	Particulate control technique[b]	Reinjection[c]	Firing rate GJ/hr	Capacity factor (percent)	Fuel characteristics		
		Hydrocarbons	Particulates	NO_x (as NO_2)	SO_2						Percent moisture	Percent ash	Percent S
98	10		1170.	8.		PS	N		17.		28	2.4	0.032
99	10		340.	<2.		DO	N		5.8		5.8	0.79	0.014
100	10		513.			DO	N		6.3		11	1.17	0.032
101	11			69.5		SS	C		110.		49.1	1.04	0.12
102	12		137.			DO	MC		54.				
103	12		238.			DO	MC		71.				
104	12		112.			DO	MC	RS	25.				
105	13	128.				SS	MC		51.[d]				
106	13	19.4				SD	N		21.[d]				
107	13	86.0				DO	N		11.[d]				
108	13	75.6				DO	N		72.[d]				
109	14				0.447	S	C		270.			1.3	0.068
110	14				0.890	S	C		160.			1.3	0.010
111	14				3.61	S	C		150.			2.5	0.060
112	14				0.92	S	C		260.			3.3	0.134
113	15			2.0			N		1.8				
114	15			60.0			N		99.				
115	15			55.0			N		33.				
116	15			5.0			N		20.				
117	15			14.2			N		25.				
118	16			47.6		SS			152.[d]	80			
119	16			61.2		SS			400.[d]	95			
121	16			57.2		SS			99.[d]	95			
122	16			86.0		SS			277.[d]				
123	16			72.2		SS			269.[d]				
124	16			72.1		SS			140.[d]	86			
125	16			46.8		SS			135.	83			
126	16			78.3		SS			123.[d]	87			
127	16			92.0		SS			109.[d]	68			
129	16			96.6		FB			32.[d]	83			
130	16			47.8		CB							

[a] Firing method:
DO -- Dutch Oven
SS -- Spreader Stoker
PS -- Pneumatic Stoker
S -- Stoker
SD -- Sander Dust
FB -- Fluidized Bed
CB -- Cyclone Burner

[b] Particulate Control Technique:
MC -- Multiclone
N -- No Control
C -- Cyclone

[c] RS -- Partial Fly Ash Reinjection
R -- Fly Ash Reinjection

[d] Steam production rate is presented in lieu of firing rate.

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APPENDIX D

METRIC CONVERSION FACTORS AND PREFIXES

CONVERSION FACTORS

To convert from	To	Multiply by
Degrees Celsius (°C)	Degrees Fahrenheit (°F)	t(°F) = 1.8 t(°C) + 32
Joule (J)	Btu	9.478×10^{-4}
Kilogram (kg)	Pound-mass (avoirdupois)	2.205
Kilojoule/kilogram (kJ/kg)	Btu/lb_m	4.299×10^{-1}
Megagram (Mg)	Ton (2000 lb_m)	1.102
Megawatt (MW)	Horsepower (HP)	1.341×10^{3}
Meter (m)	Foot (ft)	3.281
$Meter^3$ (m^3)	Barrel (bbl)	6.290
$Meter^3$ (m^3)	$Foot^3$ (ft^3)	3.531×10^{1}
$Meter^3$ (m^3)	Gallon (gal)	2.642×10^{2}
Nanogram/joule (ng/J)	lb_m/million Btu	2.326×10^{-3}
Picogram/joule (pg/J)	lb_m/million Btu	2.326×10^{-6}

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
Peta	P	10^{15}	1 Pm = 1 x 10^{15} meters
Tera	T	10^{12}	1 Tm = 1 x 10^{12} meters
Giga	G	10^{9}	1 Gm = 1 x 10^{9} meters
Mega	M	10^{6}	1 Mm = 1 x 10^{6} meters
Kilo	k	10^{3}	1 km = 1 x 10^{3} meters
Milli	m	10^{-3}	1 mm = 1 x 10^{-3} meter
Micro	μ	10^{-6}	1 μm = 1 x 10^{-6} meter
Nano	n	10^{-9}	1 nm = 1 x 10^{-9} meter
Pico	p	10^{-12}	1 pm = 1 x 10^{-12} meter